

COPPER CATALYSTS IN THE
SELECTIVE HYDROGENATION
OF SOYBEAN AND RAPESEED
OILS

LARS ERIK JOHANSSON

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AVDELNINGEN FÖR KEMISK TEKNOLOGI

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CIV ING., MLM

AKADEMISK AVHANDLING SOM FÖR AVLÄGGANDE AV TEKNISK DOKTORS-
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COPPER CATALYSTS IN THE
SELECTIVE HYDROGENATION
OF SOYBEAN AND WAPSEED
OILS
LARS ERIK JOHANSSON
CIV ING., MSc



ANALYTISK AVHANDLING SOM FÖR AVSLUTNING AV TEKNISK DOKTOR-
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COPPER CATALYSTS IN THE SELECTIVE HYDROGENATION OF SOYBEAN AND RAPESEED OILS

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The thesis consists of this summary and the following
papers, referred to in the text by their Roman numerals:

- I. Copper Catalysts in the Selective Hydrogenation of
Soybean and Rapeseed Oils: I. The Activity of the
Copper Chromite Catalyst
L.E. Johansson and S.T. Lundin
- II. Copper Catalysts in the Selective Hydrogenation of
Soybean and Rapeseed Oils: II. The Effect of a
Hydrogen Flow over Copper Chromite Catalyst
L.E. Johansson and S.T. Lundin
- III. Copper Catalysts in the Selective Hydrogenation of
Soybean and Rapeseed Oils: III. The Effect of Pressure
when Using Copper Chromite Catalyst
L.E. Johansson
- IV. Copper Catalysts in the Selective Hydrogenation of
Soybean and Rapeseed Oils: IV. Copper on Silica,
Phase Composition and Preparation
L.E. Johansson

All the papers are submitted for publication.

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INTRODUCTION

In Sweden today, the soybean and rapeseed oils are the two most important oils. A majority of the soybean oil is imported as raw oil to be processed here. The rapeseed oil, however, is mostly produced from seed grown in Sweden. After refining, a major part of the oils are subjected to catalytic hydrogenation in order to increase the stability towards oxidation. If the oil is to be used in production of margarine, the hydrogenation is performed in such a way that the melting point is extensively increased. The fat hydrogenation catalysts are usually based on nickel.

The soybean and rapeseed oils are more susceptible to autoxidation than e.g. sunflower, groundnut and cottonseed oils. This is due mainly to the presence of 2-15% linolenic acid in the triglycerides. Linolenic acid is a highly unsaturated fatty acid with 18 carbon atoms and three double bonds in the 9, 12, and 15 positions. The methylene groups situated between the double bonds are attacked by the atmospheric oxygen and unstable hydroperoxides are formed. If the percentage of the linolenic acid component is reduced by hydrogenation, the stability towards autoxidation is increased.

In 1948 it was shown by Miyake (1) that polyunsaturated fatty acid esters undergo partial selective hydrogenation over copper chromium oxide catalyst to form esters of the oleic acid serie. Esters of the oleic acid serie remain intact. The selectivity characteristics of the copper chromium oxide catalyst may be ascribed to the copper part of the catalyst and are practically independent of the type of copper catalyst. A partial hydrogenation with such a catalyst leaves fairly high amounts of essential fatty acid, *cis,cis*-9,12-octadecadienoic acid, in e.g. soybean and rapeseed oils (2). The amounts of saturated acid are not increased. From the

viewpoint of nutritional physiology, the selectivity of the copper catalysts is superior to that of the nickel catalysts but the activity is considerably lower, which increases the cost of hydrogenation.

The copper chromite catalyst was introduced as a hydrogenation catalyst by Adkins et al. in 1931 (3). This group presented a modified copper chromite catalyst, containing barium chromate as a stabilizing agent (4). In 1934 Calingeart and Edgar described a procedure for the industrial production of the copper chromite catalysts (5). In 1949 Stroupe published an X-ray diffraction study of the copper chromite catalyst (6). Since then, this catalyst system has been subjected to several investigations in connection to both hydrogenation and oxidation reactions.

The copper chromite catalyst has been used in laboratory investigations of the selective hydrogenation of vegetable oils first of all at the Northern Regional Research Laboratory (USDA), Peoria, Illinois (Koritala and Dutton): a study of mechanism (7-10), catalyst poisoning (11) and the effect of pressure (12,13). A full scale hydrogenation of soybean oil was performed in 1973 at the same laboratory (14).

The supported copper catalyst was introduced in the selective hydrogenation of fatty oils by Miyake in 1948 (1). Such catalysts were described in patent specifications from Unilever, the Netherlands (15). A report of approximately 50 supported copper catalysts was given by Koritala in 1968 (16).

Much penetrating work has been carried out to follow the reactions of the oil phase during the selective hydrogenation. With a few exceptions, e.g. the work of Okkerse et al. (17), less attention has been given to the structure of the solid phase.

The purpose of the present work has been to study the copper catalysts in connection to the hydrogenation of soybean and rapeseed oils. The copper chromite catalyst has been investigated in order to find out the active component of the copper catalysts. The resulting model of the active phase of copper has been applied in the preparation of supported copper catalysts.

The part of the work, which concerned the optimum technical conditions of the hydrogenation process over copper catalysts has been presented earlier (18).

EXPERIMENTAL PROCEDURES

Hydrogenation was carried out with technically refined and bleached soybean and rapeseed oils. After a comparative test including commercially supplied copper catalysts, two copper chromite catalysts from the Harshaw Chemical Company were chosen for the work presented in Paper I-III:

Cu-1106P (40% CuO, 47% Cr₂O₃, and 10% BaO) and Cu-1800P (51% CuO and 47% Cr₂O₃).

The hydrogenation reaction was followed by the change of the iodine value (I.V.), determined according to the Wijs method. The fatty acid composition of the oil samples was determined by GLC analyses of methyl esters, prepared from the oil samples with dimethyl carbonate and sodium methylate catalyst. The methyl esters were analyzed with a BDS column. The percentage of conjugated dienes was calculated from the UV absorption at 232 nm. The selectivity towards the linolenic acid component was calculated according to the procedure of Butterfield and Dutton (19).

The phase composition of unused and used catalyst was determined with X-ray diffraction analysis. The amount of

crystalline copper metal in the samples of used Cu-1106P catalyst was estimated using the barium chromate phase as an internal standard.

The ESCA method was used to decide the oxidation state of surface copper. The samples of used catalyst intended for ESCA measurements were washed free from fat in chloroform for 72 hr in a Soxhlet apparatus.

A mass spectrometer was used to follow the composition of occurring gaseous flows.

Hydrogenations were carried out in a 1 liter Parr apparatus type 4521. The oil to be hydrogenated and the appropriate amount of catalyst were charged into the autoclave. The oil and catalyst mixture was flushed by bubbling nitrogen gas through the oil. During the heating-up period, the oil was stirred at reduced pressure. The reaction was started by admitting hydrogen gas into the autoclave.

In a standard hydrogenation experiment, 300 g of oil was hydrogenated at a stirrer rate of 1700 rpm with a hydrogen flow through the oil of 50 liter/hr (measured after the outlet valve at 1 atm and 20°C). The standard temperature level was 185°C.

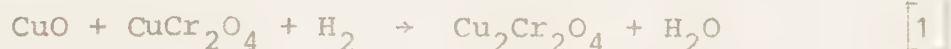
The volumetric mass transfer coefficient under the standard conditions was determined to $ka = 0.65 \text{ sec}^{-1}$. In the actual experiments, the rate of hydrogenation was so low that there was no need to correct for the influence of the external mass transfer resistance (11).

SUMMARY OF PAPERS I-IV

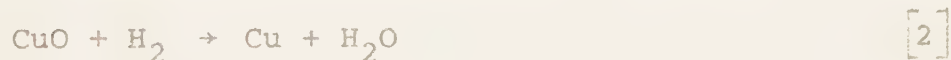
Paper I

The copper chromite catalyst is usually produced from the precipitate $\text{Cu}(\text{OH})\text{NH}_4\text{CrO}_4$ by decomposition in air at $350\text{--}500^\circ\text{C}$. Two separate crystalline phases are formed, CuO and CuCr_2O_4 (6). The material is incompletely crystallized. In the electron micrographs three dypes of particles appear, representing different stages of crystallization. The majority of the material forms aggregates of smaller particles.

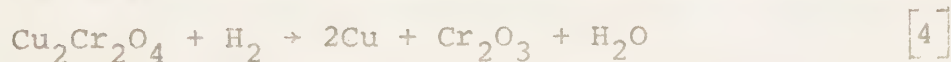
The chromite catalyst is reduced during its use. The reduction occurs during the first 40-60 min, i.e. during a period which corresponds to a normal industrial hydrogenation. Already at the first stage of the catalyst reduction, both the CuO and the CuCr_2O_4 phases are involved. In this respect, the results are consistent with the findings of Miyake (1) and Stroupe (6). The reaction



can be noted as the sum of the two reactions



The $\text{Cu}_2\text{Cr}_2\text{O}_4$ phase is reduced to copper metal and chromic oxide:



The proportion of Cu metal in the catalyst increases rather rapidly during the first 10-15 min (0.1% Cu in soybean oil, 185°C and 3 atm H_2 pressure). After a second period of Cu metal formation, about 95% of the copper has been reduced to metal. The size of the copper crystallites formed varies within the interval 80-100 Å.



The rate of reaction $-d(IV)/dt$ of a hydrogenation process with unused copper chromite catalyst varies extensively during the process. Schematically, a typical iodine value curve may be divided into three regions (Fig. 1). The reaction rate of these regions varies at three levels in the approximate ratio 6:2:1. No correlation has been found between the transition point B and the composition of the oil.

The activity changes of a catalyst during a hydrogenation run have been followed by activity measurements at a constant fatty acid composition. Already during the heating-up period prior to a hydrogenation run of soybean oil, the catalyst activity decreases to about 50%. During the process, three periods of activity appear.

The three periods of catalyst activity coincides in time with the three periods of reaction rate. This is shown in Figure 2, where the phase composition from X-ray diffraction and the oxidation state of the surface copper from ESCA are also given. The principal variations of the reaction rate can be ascribed to the changes of the catalytic activity, which are connected to the variations of the phase composition of the catalyst. The two first periods of catalytic activity are strongly bonded to the reduction of the catalyst, during which the surface layer consists of $Cu_2Cr_2O_4$ and Cu metal. A separate phase of $Cu_2Cr_2O_4$ shows no activity and the activity of Cu metal has been found to be low, especially in the presence of water. Therefore, the activity is to be ascribed to the combination of Cu and $Cu_2Cr_2O_4$.

The third period of activity arises from the reduced catalyst, in which 95% of the copper is present as metal on a Cr_2O_3 support. The remaining Cu^I ions may be important parts of the catalyst surface.

Paper II

The major part of the copper hydrogenations, which are described in the literature, has been performed in a dead-end hydrogenation system. In such a system, the reactor is supplied with as much hydrogen gas as the oil consumes and dispersion of the gas is obtained by mechanical agitation. From the preparatory experiments of this study it was concluded that the time, which is required to reduce the linolenate content of soybean oil to ca. 1%, may be reduced if the dead-end procedure is replaced with a procedure combining the mechanical agitation of the dead-end reactor with a limited flow of hydrogen through the oil. Hydrogenations using a hydrogen flow have been used earlier by others (14,20), however without discussing the benefits.

A flow of hydrogen gas through the oil and out from the autoclave may affect the conditions of hydrogenation by a) improving phase contact gas/liquid, b) maintaining the hydrogen pressure in the head-space, and c) removing water and other catalyst poisons from the oil. These three effects and their influences on the rate of reaction under test-hydrogenation conditions are discussed in the present work.

The effect of water removal is of special interest since the reduction of the copper catalyst involves the generation of water. The poisoning effect of water on the surface of reduced copper is thoroughly discussed in literature (21,22). On the other hand, water has been found to enhance the conditions of dissociative adsorption of hydrogen in systems, in which the hydrogen spillover is assumed to occur (23,24).

On the basis of mass transport experiments, the effect of improving phase contact gas/liquid is considered to be negligible at the standard conditions of the laboratory tests.

The complete reduction of the divalent copper of an unused catalyst implies the generation of ca. 0.16 mole water per kg oil and percentage unit Cu in the oil (wt-%). The reduction

water is considered to be responsible for the major part of the hydrogen dilution during a dead-end hydrogenation.

In a dead-end hydrogenation run with 0.1 wt-% Cu and 0.3 kg oil in the autoclave, the prolonging effect of hydrogen dilution, estimated from the relation between hydrogenation time and the partial pressure of hydrogen, corresponds to about 2 min, i.e. the prolongation is within the margin of errors (the time of hydrogenation in a flow run = 30 min).

The reduction water leaves the oil in two periods, reflecting the two periods of catalyst reduction. Besides the water, carbon compounds with up to six or seven carbon atoms are leaving the oil during the flow hydrogenation run. No hydrogen sulphide has been detected.

The condensates of the organic compounds show the UV-absorption of conjugated dienes, trienes and tetraenes. The spectrum obtained may be ascribed to oxidation products formed during the bleaching process. Preconjugation has a negative effect on the rate of hydrogenation. To a certain extent, that effect can be reduced by nitrogen stripping of the oil before the hydrogenation step.

A moderate water concentration of the oil phase favours the catalyst reduction while too much water retards it. The course of copper metal formation during dead-end hydrogenation is different from that of a flow hydrogenation. The marked second period of copper formation, which is found during flow conditions, is considerably weaker in the dead-end process and so is the second period of activity. When the reduction is finished, the rate of hydrogenation is lower in the presence of water than in its absence.

Table I shows the effect of a hydrogen flow on the hydrogenation time and the selectivity towards the linolenic component. Maximum effect is obtained at a flow of 50 liter H_2 /hr, at which the time which is required for an iodine value drop of

15 units is about 40% of the time in the corresponding dead-end hydrogenation. The selectivity towards the linolenate component is nearly unchanged.

The industrial application of the flow procedure corresponds to a system using hydrogen recirculation, which includes a purification train, dimensioned for a water uptake of ca. 0.3 kg water/kg copper in the catalyst charge.

Paper III

During that part of the process when the catalyst is being reduced, two hydrogen-consuming reactions are occurring at the catalyst surface. X-ray diffraction measurement on Cu-1106P catalyst, which has been reduced in a prehydrogenated soybean oil under standard hydrogenation conditions, shows that the formation of copper metal proceeds in a higher rate if no hydrogenation reaction occurs. However, the final reduction level is the same irrespective of whether hydrogenation occurs at the surface or not.

The first step of the hydrogenation process, the reaction of conjugation, requires no net supply of hydrogen. Therefore, the formation of conjugated dienes is favoured by a low supply of hydrogen at the catalyst surface. The influence of a low hydrogen concentration in the liquid phase has been shown experimentally by interruption of the hydrogen supply to the autoclave. The accumulation of conjugated dienes is not only strongly dependent of the hydrogen concentration of the oil, as was earlier known (25), but also extremely sensitive to variations of that concentration.

The conjugation reactions start immediately upon the introduction of hydrogen gas to the oil and catalyst mixture. The accumulation of conjugated dienes occurs especially over phases subjected to reduction. The accumulation over a separate CuCr_2O_4 phase is small compared to that of the

complete copper chromite catalyst. Copper metal in the form of Raney-Cu forms practically no conjugated dienes at 6 atm H_2 pressure.

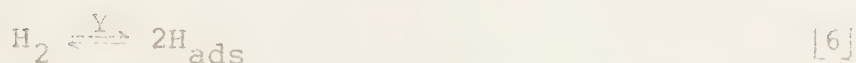
The percentage of conjugated dienes in the oil has a maximum, which decreases with the increase of pressure. Above 13 atm the accumulation over the copper chromite catalyst is low and independent of pressure.

The mean rate of hydrogenation increases with pressure up to about 6 atm, which is in accordance with the data in literature (12). The same normal relation between the rate of reaction and pressure is valid above 14 atm (Fig. 3a). The marked change of the graph at 11-12 atm/185°C and 15-16 atm/200°C resp. is ascribable to the effect of water, which cannot be avoided to the same extent in hydrogenation above the pressure level of saturated water vapour (ca. 11 atm/185°C and ca. 15 atm/200°C).

The rate maximum at 6 atm is ascribable to the activity of the oxidic surface. The contribution of the oxidic phase decreases with pressure. Above the pressure level of 12-13 atm, the hydrogenation reaction is catalyzed by the reduced form of catalyst. At 185°C, the mean rate of reaction in the interval 13-20 atm is proportional to $(p_{H_2} - 12)^{0.5}$.

The influence of hydrogen pressure on the selectivity towards the linolenic compound is small.

A reaction model is proposed, in which the catalyst surface is described as a combination between the two surfaces X and Y. The surface S is characterized as an oxidized surface, containing Cu^+ and O^{2-} ions, perhaps activated by a limited reduction to Cu metal. The surface Y is an oxide surface during the reduction, i.e. when Cu metal atoms are in close contact with adjacent oxide. The close contact is obtained by the formation of copper from the oxide phase. According to the reaction model, the hydrogenation reaction proceeds as follows:



where D is a system of two methylene-interrupted double bonds, CD is a system of two conjugated double bonds, and M is a monoene.

The dissociative adsorption of hydrogen is the rate-determining step during the periods of high catalytic activity. However, owing to the connection between the catalyst reduction and the activity, the effect of a relative hydrogen shortage on the rate of hydrogenation may be only partially eliminated by an increase of pressure within the pressure range of a normal industrial fat hydrogenation converter.

Concerning the use of the copper chromite catalyst below the pressure of 14 atm, the maximum rate of hydrogenation is obtained with an unused catalyst at 6 atm in the laboratory autoclave, which corresponds to about 8 atm in an industrial reactor with $k_a = 0.05 \text{ sec}^{-1}$.

Paper IV

Judging from the work with the copper chromite catalyst, the most ideal copper catalyst consists of small copper metal crystallites and copper atoms partially covering a layer of oxidic copper, which is resistant to further reduction.

Silica gel adsorbs copper ions from ammoniacal solutions in the form of tetrammine complex (26-30). One type of copper ammine polysilicate is formed. The copper adsorbed in this way is more tightly bonded to the gel than in the case of impregnation from neutral solutions,

The method of copper adsorption onto silica gel from ammoniacal solution has been used by Koritala in the preparation of copper catalysts for the hydrogenation of soybean oil (31). Here the method of preparation has been modified for the rapeseed oil processing.

The principal method of preparation is as follows: An ammonium hydroxide solution is added to an aqueous solution of copper nitrate. The copper hydroxide precipitate is redissolved. The silica gel is added to the copper solution and part of the blue ions are adsorbed onto the gel. The remainder of the copper ions is precipitated onto the gel as copper hydroxide when the solution is diluted with water. The procedure is repeated once. The pale blue catalyst is dried over night at 110°C and calcined at 350°C for 2 hr.

The composition of the adsorption solution was varied within this study. A catalyst material containing 17% Cu was chosen for a more penetrating study.

The calcined catalyst material contains small CuO crystal needles, which are visible at the electron micrographs. A broad peak is found in the X-ray diffraction spectra. The BET surface area of the emerald-green material is ca. $350 \text{ m}^2/\text{g}$.

In soybean oil the copper content is reduced to Cu_2O and Cu metal, even at 3 atm H_2 pressure. In rapeseed oil, however, the same phase composition is obtained first at hydrogenation above 20-25 atm.

The curve activity versus reaction time of a Cu/SiO_2 catalyst, used in soybean oil at 3 atm and 185°C , show three periods of activity. This curve is similar to that obtained with the use of the copper chromite catalyst in soybean oil. The activity curve in rapeseed oil at 6 atm H_2 pressure shows only two periods of activity. Also in this respect, the Cu/SiO_2 catalyst behaves similarly to the chromite catalyst.

The effect of the H_2 pressure on the reaction rate in rapeseed oil is shown in Figure 3b. In the pressure range below 20 atm, the hydrogenation proceeds for the most part over an oxidic surface, i.e. a surface containing monovalent copper. A maximum rate is obtained at 6 atm. The effect of water is as clear as was earlier shown for the copper chromite catalyst (III). The mean rate of reaction over the grey-black catalyst surface increases with pressure. In the interval $20 < p_{H_2} < 32$, the mean rate of reaction, $\Delta(IV)=15$, is proportional to $(p_{H_2} - 14.5)^{0.5}$.

The selectivity value is only slightly dependent on the H_2 pressure.

In the proposed reaction model (III), the catalyst surface is described as a combination of the two surfaces X and Y, which may be characterized by showing predominantly oxidic and metallic properties respectively. Here, the method of catalyst preparation has been modified on the basis of the reaction model. The first copper ions that are adsorbed onto the silica gel are bonded directly to the support material. These atoms are assumed to constitute the oxidic part of the partly reduced catalyst. The strength of the bonds between the copper ions and the support increases with the excess of the NH_4OH in the adsorption solution.

The catalyst activity per unit Cu increases with the excess of NH_4OH . If too strong an alkaline solution is used, it results however in an almost inactive catalyst.

Another possibility for improving the activity per g of Cu charged consists of combining two catalyst materials, one is constructed to produce conjugated dienes (the oxidic component) and the other one to hydrogenate the conjugated dienes produced (the copper metal component).

Experiments were carried out with mixtures of two Cu/SiO₂ catalysts; type A, in which the copper is more strongly bonded to the support and type B in which the average bond between Cu and the support is weaker. The time required for an iodine value drop of 15 units in rapeseed oil with a catalyst mixture, where the ratio between the amounts of copper charged as A and B was 2:1, was 47% shorter than if the same amount of copper was charged as catalyst A only and 34% shorter than if all the copper was charged as catalyst B.

The accumulation of conjugated dienes during the periods of high catalyst activity indicates a relative hydrogen shortage on the catalyst surface. Addition of metals other than copper may increase the dissociative adsorption of hydrogen. Here, additions of chromium, cobalt, zinc and silver were made in order to increase the rate of hydrogen adsorption. Only the addition of cobalt gave an enhanced catalyst activity. The addition of nickel was avoided due to the risk of reactor contamination.

The Cu/SiO₂ and the Cu-1106P catalysts are rather equivalent in the respect of soybean oil, but the Cu/SiO₂ type offers considerable advantages in the hydrogenation of rapeseed oil. The order of precedence of the different Cu/SiO₂ catalysts is not absolute, but may vary depending on the type and concentration of dominating catalyst poisons. The poisoning effect of volatile oxidation products is lower with the use of Cu/SiO₂ catalysts than with the copper chromite catalyst.

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TABLE I

The effect of a hydrogen flow on the hydrogenation product.

(Cu-1106P, 0.2 wt-% Cu in the oil, 6 atm, and 185 C).

Oil	Flow l/hr	Reaction time min	IV (Wijs)	GLC Composition		trans %	Conj. dienes %	S ^c _{Ln}
				C18:0	C18:1			
C18:2 ^a C18:3 ^b								
Soybean oil	-	-	131.5	3.8	22.1	53.0	8.2	-
	0	35	117.0	3.8	32.6	49.9	1.1	14.2
	12	35	114.6	4.0	33.8	48.9	0.8	14.4
	24	20	116.0	3.9	32.8	49.1	1.0	14.4
	50	20	113.3	3.7	34.8	47.9	1.1	11.0
Rapeseed oil	-	-	111.4	1.1	36.0	19.6	10.8	-
	0	90	96.0	1.1	40.4	22.7	2.4	11.4
	10	70	95.6	1.2	41.9	22.7	1.3	11.7
	25	50	96.8	1.1	41.0	23.0	2.4	10.8
	50	50	96.7	1.1	41.0	22.6	2.1	11.4

^a Does not include conjugated dienoates.

^b Includes conjugated dienoates.

^c Calculated from the GLC compositions.

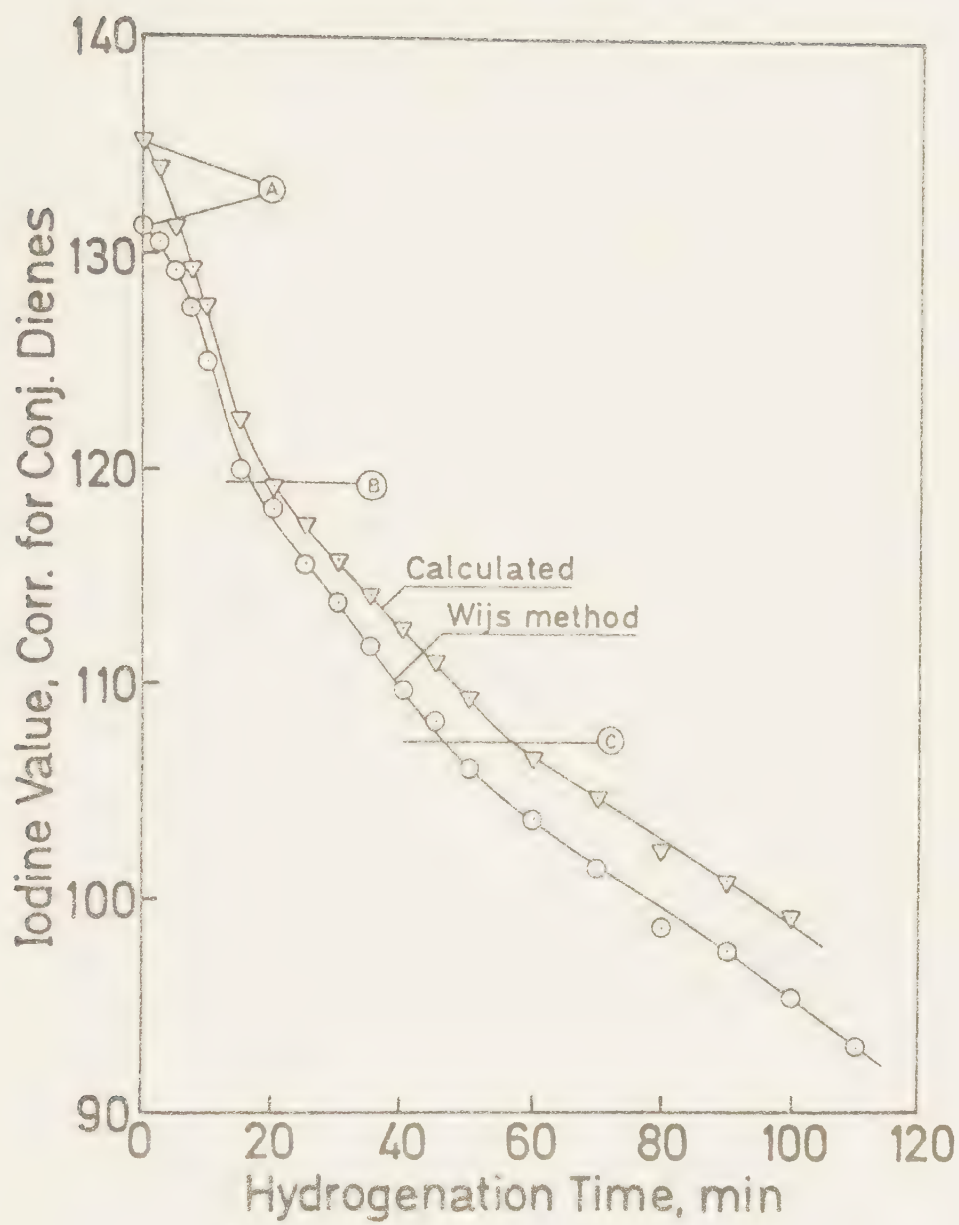


FIG. 1. Iodine value versus reaction time in the hydrogenation of soybean oil with copper chromite catalyst (Cu-1106P, 0.1 wt-% Cu in the oil, 3 atm H_2 pressure, and $185^\circ C$).



X-ray	CuO CuCr ₂ O ₄	Cu Cu ₂ Cr ₂ O ₄	Cu
ESCA	Cu ^{II}	Cu ⁰ Cu ^I	Cu ⁰ (Cu ^I)

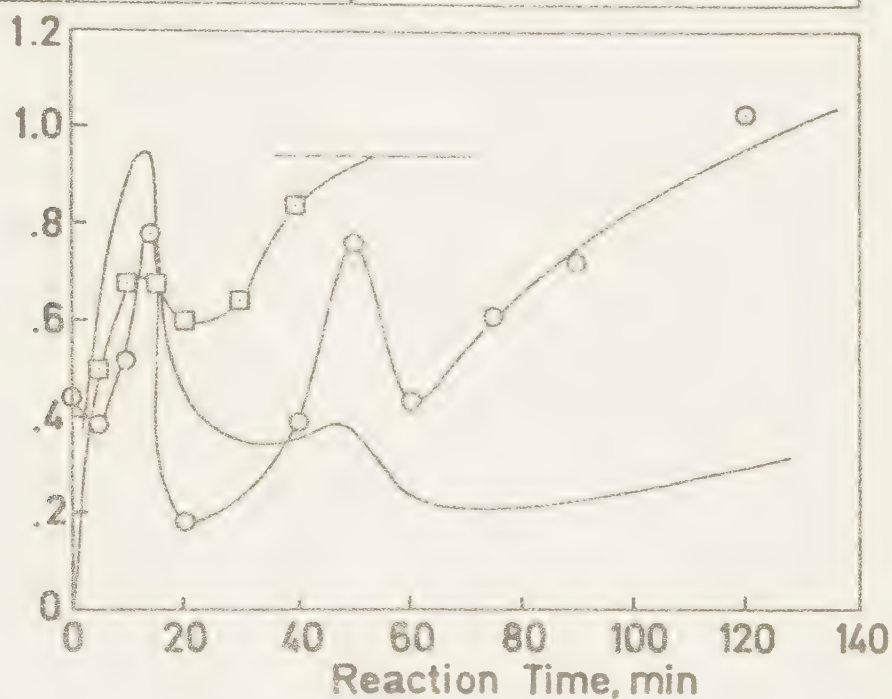


FIG. 2. Hydrogenation of soybean oil with copper chromite catalyst (0.1 wt-% Cu in the oil, 3 atm and 185°C)

a) Phase composition (Cu-1106P) and surface copper (Cu-1800P)

b) Cu-1106P:

- Hydrogenation rate $-d(IV)/dt, \text{ min}^{-1}$
- Relative catalyst activity (const. fatty acid comp.)
- Fraction of Cu as Cu metal from X-ray diffraction

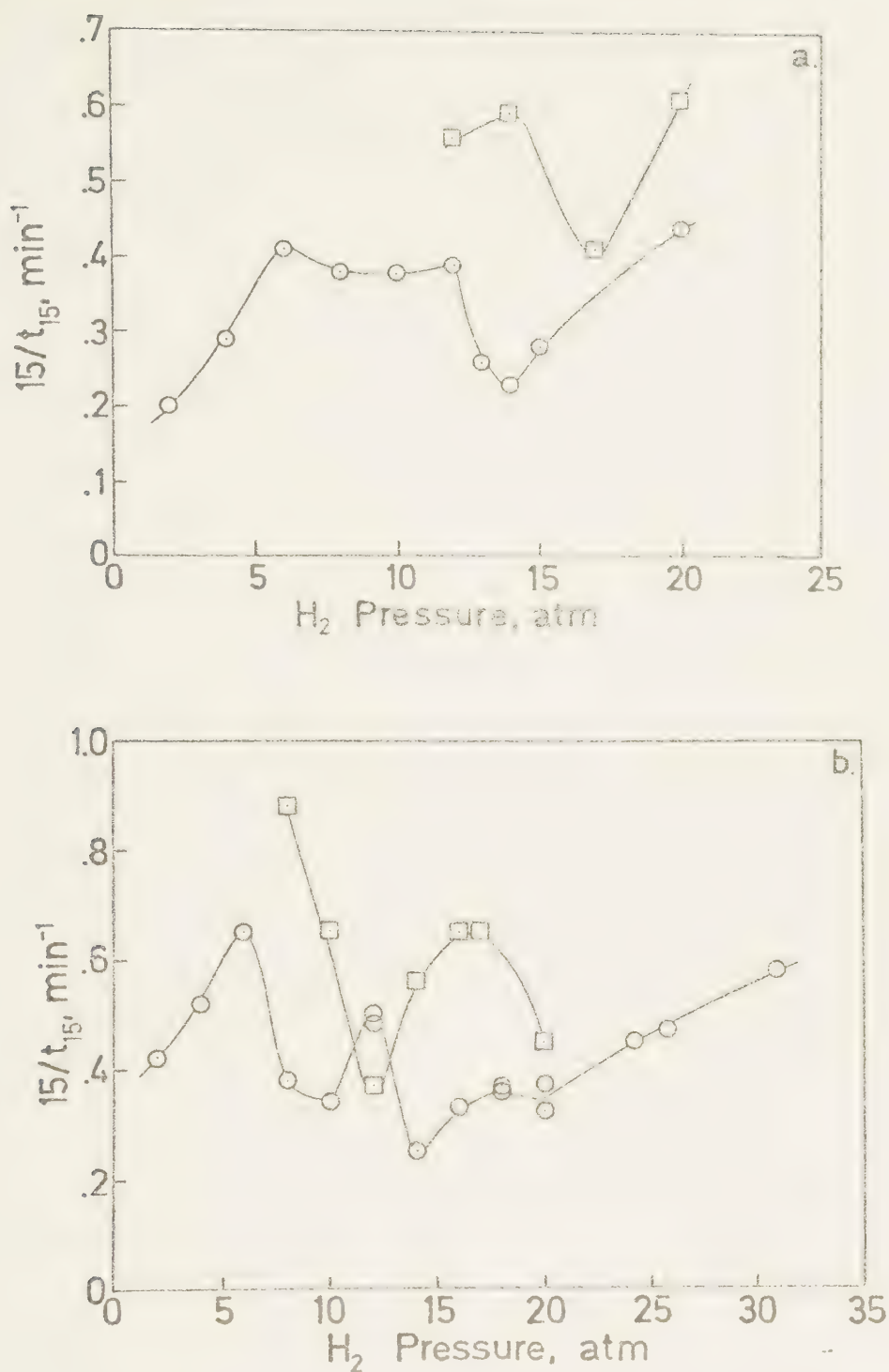


FIG. 3. Effect of pressure on the mean rate of reaction in the hydrogenation of
a) soybean oil with copper chromite catalyst (Cu-1106P, 0.05 wt-% Cu in the oil
b) rapeseed oil with Cu/SiO₂ catalyst (Cu/SiO₂ with 17% Cu, 0.12 wt-% Cu in the oil);
Reaction temperature (○) 185°C and (□) 200°C.

COPPER CATALYSTS IN THE SELECTIVE HYDROGENATION OF SOYBEAN
AND RAPESEED OILS: I. THE ACTIVITY OF THE COPPER CHROMITE
CATALYST

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Copper Catalysts in Selective Hydrogenation of Vegetable oils.

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ABSTRACT

In the hydrogenation of soybean and rapeseed oils with an unused copper chromite catalyst, the rate of reaction $-d(IV)/dt$ varies extensively with time. These variations are ascribable to the changes of the phase composition of the catalyst during its reduction. This reduction is not restricted to an initial period but proceeds in two steps during the major part of a normal hydrogenation for the reduction of the linolenate content of the oil. The variations of the catalyst activity, followed by experimental measurements, have been related to the changes of the catalyst composition.

INTRODUCTION

The most selective catalysts during the reduction of the linolenic compound in fatty oils such as soybean and rapeseed oils are copper catalysts. Monoenes are not reduced which is why the hydrogenation may be performed without increasing the amount of saturates in the oil (1,2). Different copper catalysts have been tested and the selectivity characteristics are practically independent of the type of catalyst. These properties may therefore be ascribed to the copper part (2). Whether it is the elementary form of copper or an oxidized form that contributes most to the activity of the catalyst in selective hydrogenation is however still under discussion.

Adkins et al. (3,4) found in 1931 that the copper content in the copper chromite catalyst, prepared according to Lazier, was reduced from the divalent state to the monovalent or the elementary state during its use as a hydrogenation catalyst. The reddish compound formed was inactive in hydrogenation reactions (5). They presented a modified copper chromite catalyst containing barium chromate as a stabilizing agent (4). The active form of copper, according to Adkins et al., should thus be copper(II). Koritala and Dutton hydrogenated soybean oil with sodium borohydride-reduced catalysts (1). A black precipitate, presumably copper(II)oxide, turned red after partial reduction of the oil and then became inactive. Addition of chromium stabilized the catalyst.

Okkerse et al. (2) used a Cu-Mg-SiO_2 catalyst for soybean oil hydrogenation. The activity of this catalyst was studied in a vapour phase hydrogenation of cyclohexene in order to avoid the diffusion limitation of a liquid phase hydrogenation. The activity was found to increase while decreasing the mean state of oxidation of the copper catalyst. This indicates that the active center consist of copper metal crystallites.

Derouane et al. (6) studied a similar catalyst Cu-MgO in the hydrogenation of ethylene. The copper oxides, the metallic copper, or the magnesia oxide itself showed no or minimal activity in comparison to the active catalyst. On the basis of the ESR and kinetic data, surface Cu^{2+} ions were proposed as the active species.

The opposing views in literature on the active species of the hydrogenation catalysts based on copper may partly depend on the fact that copper catalysts are used for hydrogenation under quite varied conditions. The copper chromite catalyst was originally tested by Adkins at hydrogen pressures above 100 atm. Much work has been done at these high pressure levels. The general opinion seems to be in accordance with the theory of Rabes and Schenck (7) that the active substance in copper chromite catalysts at high pressure levels is the metallic copper formed during the hydrogenation. The selective hydrogenation of vegetable oils is normally performed at hydrogen pressures lower than 10 atm under conditions in which the rate of catalyst reduction is lower and, consequently, an oxidized state of copper may contribute to the activity of the catalyst.

The reaction rate during a fat hydrogenation process with a new, unspent copper catalyst varies considerably. To a certain extent, this effect is due to the changes of the fatty acid composition of the oil. Vigneron et al. (8) have noted that the activity of the copper chromite catalyst was high during linolenate reduction but diminished quickly after the linolenate content dropped to ca. 1%. On the other hand, Koritala et al. (9) have reported that if linolenate and linoleate isomers are reduced separately, the hydrogenation rates are nearly equal.

Before use, the copper chromite catalyst consists essentially of two phases, copper(II)oxide and copper(II)chromite (10). The reduction during its use as a hydrogenation catalyst depends on the conditions, but when completely reduced, it consists of metallic copper on Cr_2O_3 (7, 11). This part of our study on the selective hydrogenation of soybean and rapeseed oils concerns the connection between the reduction of the copper chromite catalyst and the catalytic activity.

EXPERIMENTAL PROCEDURES

Material

Hydrogenation was carried out with commercially refined and bleached soybean and rapeseed oils. With respect to the erucic acid content, the latter oils were of medium quality, containing about 17% erucic acid ester.

Two commercially supplied copper chromite catalysts from Harshaw Chemical Company have been used. Normally, Cu-1106P

(40% CuO, 47% Cr₂O₃ and 10% BaO) was used due to its high activity. But in experiments including ESCA and electron microscopy, Cu-1800P (51% CuO and 47% Cr₂O₃) containing only two crystalline phases was used.

Analytical Methods

Methyl esters were prepared from oil samples with dimethyl carbonate and sodium methylate catalyst. The methyl esters were analyzed with a 9 ft. x 1/8 in. stainless steel column packed with 7% BDS on 80/100 Chrom W and a flame ionization detector.

Iodine values were determined according to the Wijs method (12). The percentage of conjugated dienes was calculated from the UV absorption at 232 nm (12). When specified in the diagram, the effect of conjugated dienes on the volumetric iodine value has been estimated to $0.86 \times (\% \text{ conjugated dienes})$ on the basis that a system of two conjugated double bonds only adds one halogen molecule. The effect of the conjugated dienes on the calculated iodine value has been estimated with the assumption that all conjugated diene molecules have the same retention time as non-conjugated trienes.

The X-ray diffraction analyses were performed with a Philips PW 1050/25 diffractometer (Cu-K radiation, 45 kV and 24 mA). Using the barium chromate phase as the internal standard, the amount of crystalline copper metal in the samples of used Cu-1106P catalyst had been estimated as follows: the diffraction angle interval $40.8 - 45.0^\circ 2\theta$ was scanned by steps of $0.05^\circ 2\theta$. The number of pulses during 1 minute was registered. The interval

42.5 - 45.0 $^{\circ}2\theta$ (A) represents the highest interference of copper metal (111) and copper(II)chromite (400). The interval 40.8 - 42.4 $^{\circ}2\theta$ (B) represents the highest interferences of barium chromate (Fig. 1). The amount of copper metal was estimated from the numbers of pulses N_A and N_B , with corrections for background intensities. Calibration was performed using mixtures of copper metal (electrolytic) and an unused catalyst as standard substances.

The ESCA measurements were performed with an AEI ES 100 electron spectrometer equipped with a hemispherical electrostatic analyzer. Oil pumps fitted with cold traps produced a vacuum of 10^{-7} Torr during the measurements. All spectra were obtained with Al K-radiation (1486.6 eV). The catalyst samples were placed on a platinum gauze during the measurements. The spectra obtained were interpreted with the help of the spectra given by Schön (13).

To make the ESCA measurements possible, the samples of used catalyst intended for ESCA studies were washed free from fat in chloroform p.a. for 72 hours in a Soxhlet apparatus. To prevent oxidation as much as possible, the catalyst samples were kept in chloroform and applied to the platinum gauze as a chloroform slurry just before placing it in to the ESCA apparatus.

Equipment and Operating Procedures

Hydrogenations were carried out in a 1 liter Parr apparatus 4521. The oil to be hydrogenated and the appropriate amount

of catalyst were charged into the autoclave. The oil and catalyst mixture was flushed with nitrogen by bubbling the gas through the oil. During the heating-up period, the oil was stirred at reduced pressure (ca. 6 Torr). The reaction was started by admitting hydrogen gas into the autoclave.

Oil samples were taken out in nitrogen gas and was immediately cooled to 0 C to prevent oxidation. The catalyst and the oil were separated in a centrifuge at 5000 rpm in nitrogen.

In all the experiments described here, 300 g oil was hydrogenated at a stirrer rate of 1 700 rpm and with a hydrogen flow through the oil of 50 liter/hr (measured after the outlet valve at 1 atm and 20 C).

According to the mass transfer conditions in this study, the volumetric mass transfer coefficient was found to be $k_a = 0.65 \text{ sec}^{-1}$. This has been determined with the use of a nickel catalyst according to a method described by Pihl and Schöön (4). By using that value of k_a , the concentration difference of hydrogen across the transport film near the gas bubbles, could be estimated. In the majority of the experiments, the rate was so low that there was no need to correct for the influence of the external mass transfer resistance. The highest rate obtained corresponded to a concentration difference of about 6% of the hydrogen solubility at the actual pressure level.

RESULTS

The Reaction Rate Regions of the Hydrogenation Process

The rate of reaction $-d(IV)/dt$ of a hydrogenation process with unused copper chromite catalyst decreases after about 20 minutes. This is demonstrated by a number of graphs of soybean oil hydrogenation with varying amounts of Cu-1106P catalyst (Fig. 2). No correlation has been found between the position of the transition point B and the composition of the oil, neither with respect to iodine value nor triene content. The iodine value drop of part AB in the process is however proportional to the amount of catalyst, which indicates a connection between the typical shape of the iodine value graphs and the solid phase (Fig. 3).

For a rough estimation of the changes in the rate of reaction, the iodine value graphs may be divided into three periods. The reaction rate $-d(IV)/dt$ of the three parts AB, BC and CD varies at three levels in the approximative ratios 6:2:1. The first part AB includes a minor induction period even with increased amounts of catalyst.

The iodine value graph of a hydrogenation with the Cu-1106P catalyst (0.1 wt-% Cu in the oil) at 185 C and 3 atm H_2 pressure which were the conditions used in several experiments in this report was determined by frequent samplings of oil. The iodine values of these samples were determined both according to the Wijs method and calculated from the GLC-composition (Fig. 4). The shape of the iodine value curve was found to be

independent of the method used. The curve (Wijs method) was derivated graphically, and the three periods of relatively high reaction rate appeared more distinctly (Fig. 5).

Changes of the Catalyst Activity during the Hydrogenation

Since the mass transfer resistance may be neglected in these experiments, the reaction rate $-d(IV)/dt$ at constant temperature and hydrogen pressure is a function of the catalyst activity and the fatty acid composition of the oil. The activity of the catalyst at different stages of reduction has been determined directly at constant fatty acid composition according to the following procedure:

A number of hydrogenation runs with unused catalyst is interrupted at different reaction times. The catalyst lot of each run is separated from the oil in a centrifuge at 6 000 rpm and charged into a portion of the original oil. The activity of each catalyst sample is estimated as $1/t_y \text{ min}^{-1}$, where t_y is the time required for an iodine value drop of y units in the second hydrogenation run. The influence of the oil composition and the reduction water is thus eliminated. The activity of the catalyst samples is given in relation to the activity of the unused catalyst under the conditions of the second run.

A too low value of the quantity y implies an uncertain activity value. A too high value of y implies a risk of missing a sharp activity period. Here the catalyst activities have been measured at 6 atm and 185 C with 3.0 iodine value units. The reaction time $t = 0$ means that the hydrogenation process was

interrupted just before the moment when hydrogen gas normally is introduced into the converter. Aside from a minor loss of catalyst material during the experimental work, the activity reduction of the heating-up period includes the effect of initial catalyst poisoning.

The activity of the Cu-1106P was found to decrease to about 50% during the heating-up period prior to a hydrogenation run of soybean oil (Fig. 6). The three periods of activity which occur correspond to the three regions of reaction rate appearing in Figure 5. The third activity period represents the final state of the catalyst.

The corresponding curve of the same catalyst used in rapeseed oil at 6 atm H_2 pressure, which was determined for the time interval 0 - 60 minutes, is similar to that of soybean oil in the respect of the second activity maximum. The first maximum is considerably lower at $y = 3$.

The three regions of relatively high reaction rate which were detected in the derivation of the iodine value graph, thus, correspond to three periods of higher catalytic activity. The explanation for the variation in catalyst activity is found in the changes of the catalyst composition during the hydrogenation process.

The Phase of the Copper Chromite Catalyst

The copper chromite catalyst is usually produced from the precipitate $\text{Cu}(\text{OH})\text{NH}_4\text{CrO}_4$ by decomposition in air at 350-500 C for about 2 hours. It is clear from the X-ray diffraction analysis that two separate crystalline phases are formed, CuO and CuCr_2O_4 (10).

The Cu/Cr ratio of the Cu-1800 catalyst is consistent with that of a catalyst prepared from the precipitate $\text{Cu}(\text{OH})\text{NH}_4\text{CrO}_4$. Approximately 63 wt-% of the material is insoluble in hot 6 N HCl and, thus, constitutes the CuCr_2O_4 phase. From the amounts of copper and chromium leached in the acid solution it follows, that about 15 wt-% of the chromium does not form the CuCr_2O_4 compound. The intimate contact between the CuO and the CuCr_2O_4 phases is clear from the fact that the catalyst material, when heated to 960 C for 5 hours, reacts to $\text{Cu}_2\text{Cr}_2\text{O}_4$ in a solid phase reaction. After such a treatment, only about 5% of the copper present is still soluble in hot 6 N HCl.

Three different types of particles appear in the electron microscopy pictures of the unused Cu-1800P (Fig. 7). The majority of the material forms aggregates of particles. The appearance of the large, long and thin particles is similar to that of the crystals which constitute the original precipitate. The third type is somewhat smaller and more compact particles, which partly exist in direct contact with the aggregates.

The larger particles dissolve in 6 N HCl. At first glance, the aggregates are resistant to the HCl leaching. However, a careful

study of the changes within the granular structure reveals the existence of small soluble crystallites which thus constitute the CuO phase.

The different types of particles represent different stages in the rearrangement reaction. The aggregates correspond to the formation of copper oxide and copper chromite, while the particles which dissolve in HCl solution represent the least crystalline material. Consequently, two forms of copper metal are formed during the catalyst reduction. The metal formed within the aggregates arises from crystalline phases and are distinguishable from the metal formed from the more amorphous copper chromium oxides of the other types of particles.

Changes of Phase Composition shown by X-ray Diffraction and ESCA measurements

In order to find the connection between the changes of the phase composition and the catalyst activity, X-ray diffraction analysis and ESCA measurements have been used to investigate catalyst samples in the hydrogenation of soybean oil at 3 atm and 185 C. The comparatively low hydrogen pressure was used with the intention of obtaining a slow catalyst reduction.

The samples for the X-ray diffraction analysis represented different reaction times of a hydrogenation with Cu-1106P (0.1 wt-% Cu, 185 C and 3 atm). The proportion of copper metal in the catalyst increases rather rapidly during the first 10-15 minutes (Fig. 8). Simultaneously the diffraction patterns of copper(II)oxide diminishes. No patterns of copper(I)oxide have been observed and only weak, broad patterns of copper(I)chromite.

The curve showing the fraction of copper in metal versus the reaction time passes a maximum at about the same time as the hydrogenation process passes point B. The highest level is reached at about the same time as the point C is passed.

The shape of the Cu^0 graph has been found significant and independent of the method used for valuating the intensities of the interference in the diffraction spectra. The highest level of crystalline copper metal in the figure, representing about 95 wt-% of the existing copper present, has been determined from X-ray diffraction analysis of a catalyst sample reduced during use in soybean oil at 20 atm for 120 minutes. The size of the copper crystallites formed varies within the interval 80-100 Å, determined from the peak broadening at $43.3^\circ 2\theta$.

The ESCA signals arise from a surface layer about 20 Å thick. Provided that the catalyst is clean from fat, information is obtained from the part of the catalyst in contact with the oil. The samples investigated here represent a hydrogenation during the same conditions as the hydrogenation above. However, the Cu-1800P catalyst was used instead of the Cu-1106P containing also a BaCrO_4 phase.

Figure 9 shows a wide scan electron spectrum from the original catalyst at 25 C. Two sections are used at the interpretations: the $\text{Cu}2p_{3/2}$ peak with the adjacent satellite peak (Fig. 10) and the $\text{L}_3\text{M}_{4,5}\text{M}_{4,5}$ Auger electron spectra (Fig. 11).

The satellite peak typical of the Cu^{II} ions is present only in the spectrum of the original catalyst. The peak width of the $\text{Cu}2p_{3/2}$ decreases with the reaction time, which indicates the reduction to Cu^0 over Cu^{I} .

The Auger spectrum of the sample, representing a reaction time of 5 minutes, corresponds to the spectrum of Cu^{I} .

The Auger spectrum of the 50 minutes sample shows the typical resolved fine structure of Cu^0 with a minimal contribution from Cu^{I} . This contribution may arise from an air-oxidized surface.

Changes of the Phase Composition from Solubility Data

Samples of unused and used Cu-1106P catalyst (0.1 wt-% Cu in soybean oil, 3 atm and 185 C) were leached by turn in hot 6 N HCl and in a hot 8:3 mixture of concentrated sulphuric acid and 85% ortho-phosphoric acid. The amounts of copper dissolved in the two leaching steps were determined by atomic absorption spectroscopy. (The composition of the acid mixture is from reference 15.)

The HCl fraction of the catalyst copper increases during the first minutes of the hydrogenation from 59% to about 95% (Fig. 8). Simultaneously the $\text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$ fraction decreases from 41% to about 5%. Obviously the CuCr_2O_4 phase is drastically changed already during the initial stage of the catalyst reduction. Copper(I)chromite, produced from the $\text{CuO} \cdot \text{CuCr}_2\text{O}_4$ compound by heating at 960 C for 5 hours, dissolves very slowly in 6 N HCl. A monovalent copper chromite phase with a disturbed crystal pattern may behave otherwise. Therefore the

result does not exclude the existence of a reduction intermediate, consisting of $\text{Cu}_2\text{Cr}_2\text{O}_4$ and giving a broad peak in the X-ray diffraction spectra. $\text{Cu}_2\text{Cr}_2\text{O}_4$ dissolves in the acid mixture.

The Behaviours of the Different Copper Phases

The copper(II)oxide phase of a lot Cu-1800P catalyst was removed in hot 6 N HCl. The X-ray diffraction spectrum showed no patterns of copper(II)oxide. The ratio Cu/Cr of the surface was equal to that of the inner part of the grains, exposed by grinding (ESCA).

The effect of removing the CuO phase has been studied earlier in other hydrogenation systems, but not in fat hydrogenation (16,17). Questions have been raised as to whether the remaining chloride ions from the HCl leaching might not cause catalyst poisoning. Here the ESCA has shown that the amount of chlorine at the surface of the catalyst grains was unchanged throughout the leaching procedure.

The CuCr_2O_4 powder was tested for catalytic activity in rapeseed oil (6 atm and 185 C). The first activity period of the original catalyst was replaced with an induction period, of about 20 minutes (Fig. 12). Maximum activity, corresponding to about one fourth of the activity of the whole catalyst, was obtained after 40 minutes.

A separate phase of CuCr_2O_4 is reduced at a lower rate than the CuCr_2O_4 phase of the complete catalyst. The importance of the effect of the mixing is further clarified by the fact that

the hydrogenation activity of copper oxide is low. For instance, the iodine value decrease of a very easily reduced soybean oil in a hydrogenation with 2.5 g of CuO at 6 atm and 185 C for 70 minutes was only ca. 4 units.

Copper metal, which has been tested for activity in the form of electrolytic Cu and Raney-Cu ($18 \text{ m}^2/\text{g}$), shows low activity. The selectivity towards the linolenate component of soybean oil is to be compared with that of nickel catalysts. The substances Cu_2O and $\text{Cu}_2\text{Cr}_2\text{O}_4$ show no or minimal activity. The finely divided copper metal and copper oxide mixture obtained by decomposition of copper(II)oxalate shows no activity at all. Our conclusion is that no one of these separated phases can be the cause of the activity found in the fat hydrogenation with the copper chromite catalyst. The CuO and Cu_2O components are immediately reduced to metal, at least as far as the surface layer is concerned. The $\text{Cu}_2\text{Cr}_2\text{O}_4$ phase, produced at 960 C, is stable for reduction at 6 atm H_2 pressure and 185 C (X-ray diffraction).

Specific Surface Area Measurements

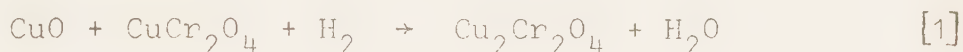
Samples corresponding to different times of reaction in a hydrogenation of soybean oil with Cu-1800P catalyst (0.2 wt-% Cu in the oil, 6 atm and 185 C) were washed in a Soxhlet apparatus until a new portion of chloroform showed no absorption at 220 nm in the UV spectrum. The amount of remaining fat within the catalyst pores was estimated from an analysis of the carbon to be about 3.5 wt-%, which corresponds to less than 5% of the pore volume. The specific surface areas of the samples were determined according to the BET method (Table I).

The reduction of the catalyst occurs without any significant increase of the specific surface area. The effect of sintering on the activity of the catalyst is of minor importance.

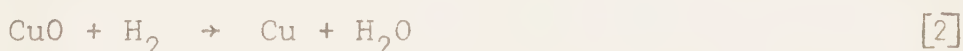
DISCUSSION

The variations of the catalytic activity during a hydrogenation process with an unused copper chromite catalyst is ascribable to the different stages of the catalyst reduction.

The first stage of the catalyst reduction involves both the CuO and the CuCr_2O_4 phases. The two phases exist in contact with each other, which facilitates the reduction of the CuCr_2O_4 phase. Stroupe (10) proposed a low temperature version of the reaction between CuO and CuCr_2O_4 occurring above 900 C resulting in the formation of $\text{Cu}_2\text{Cr}_2\text{O}_4$:



This reaction can be noted as the sum of the two reactions:



Stoichiometrically ca. 83% of the existing copper in the Cu-1106P catalyst can react in this way. The $\text{Cu}_2\text{Cr}_2\text{O}_4$ phase formed is then reduced to copper metal and chromic oxide:



The excess of CuO is reduced to metal according to the reaction [2] without any connection with the CuCr_2O_4 phase.

The decrease in the amount of copper metal, registered by the X-ray diffraction analyses, could be the result of reaction 3 . However, this is inconsistent with the solubility experiments, which seems to show that no CuCr_2O_4 phase remains at that stage.

The third period of catalyst activity is to be ascribed to the reduced catalyst, in which about 95 % of the copper exists as $\text{Cu/Cr}_2\text{O}_3$. That component contributes to the activity to a greater extent first in a stage, where water no longer is being generated. This is in agreement with the fact that water is known first of all as a poison to the reduced copper catalyst. The main part of an industrial hydrogenation process with unused catalyst with a reaction time of about 60 minutes is however performed with activity belonging to the first two periods.

The Cu^{II} ions on the catalyst surface are reduced already during the first minutes of the hydrogenation process. During the catalyst reduction the surface layer consists of $\text{Cu}_2\text{Cr}_2\text{O}_4$ and Cu metal. A separate phase of $\text{Cu}_2\text{Cr}_2\text{O}_4$ shows no activity and the activity of Cu metal has been found to be low, especially in the presence of water. Activity is thus to be ascribed to the combination of Cu and $\text{Cu}_2\text{Cr}_2\text{O}_4$. The catalytic activity is strongly bonded to the reduction of the catalyst. The active species may consist of especially activated copper atoms, e.g. coordinatively unsaturated copper.

The results presented here combine some of the apparently opposing views of literature on the active phase of the copper chromite catalyst by showing that two separate levels of catalyst reduction possess activity.

ACKNOWLEDGEMENTS

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TABLE I

The BET surface of Cu-1800P catalyst samples from a soybean oil hydrogenation at 6 atm and 185 C.

Reaction Time min	BET-surface m^2/g
-	32.1
0	32.2
5	31.5
10	31.9
20	31.9
35	30.0
90	30.7

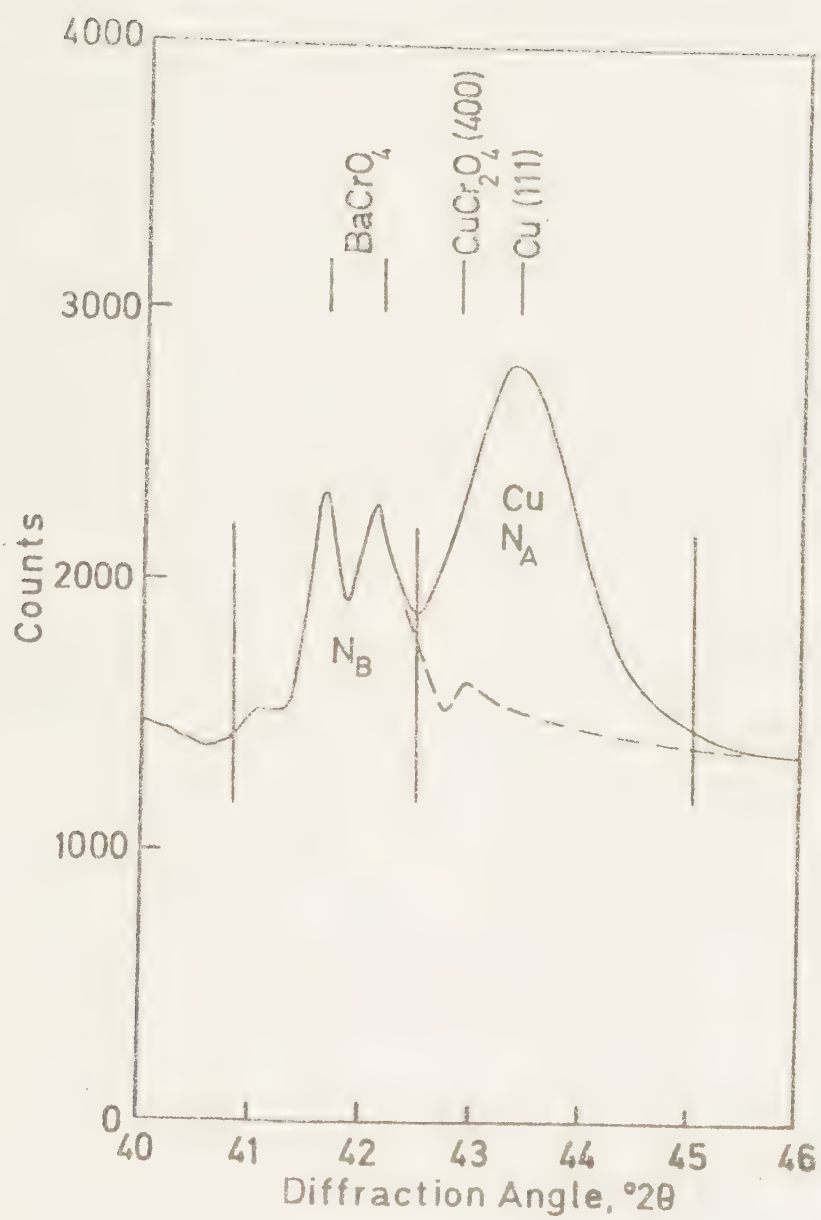


FIG. 1. X-ray diffraction spectrum of used Cu-1106P catalyst showing the method of quantitative copper metal determination.



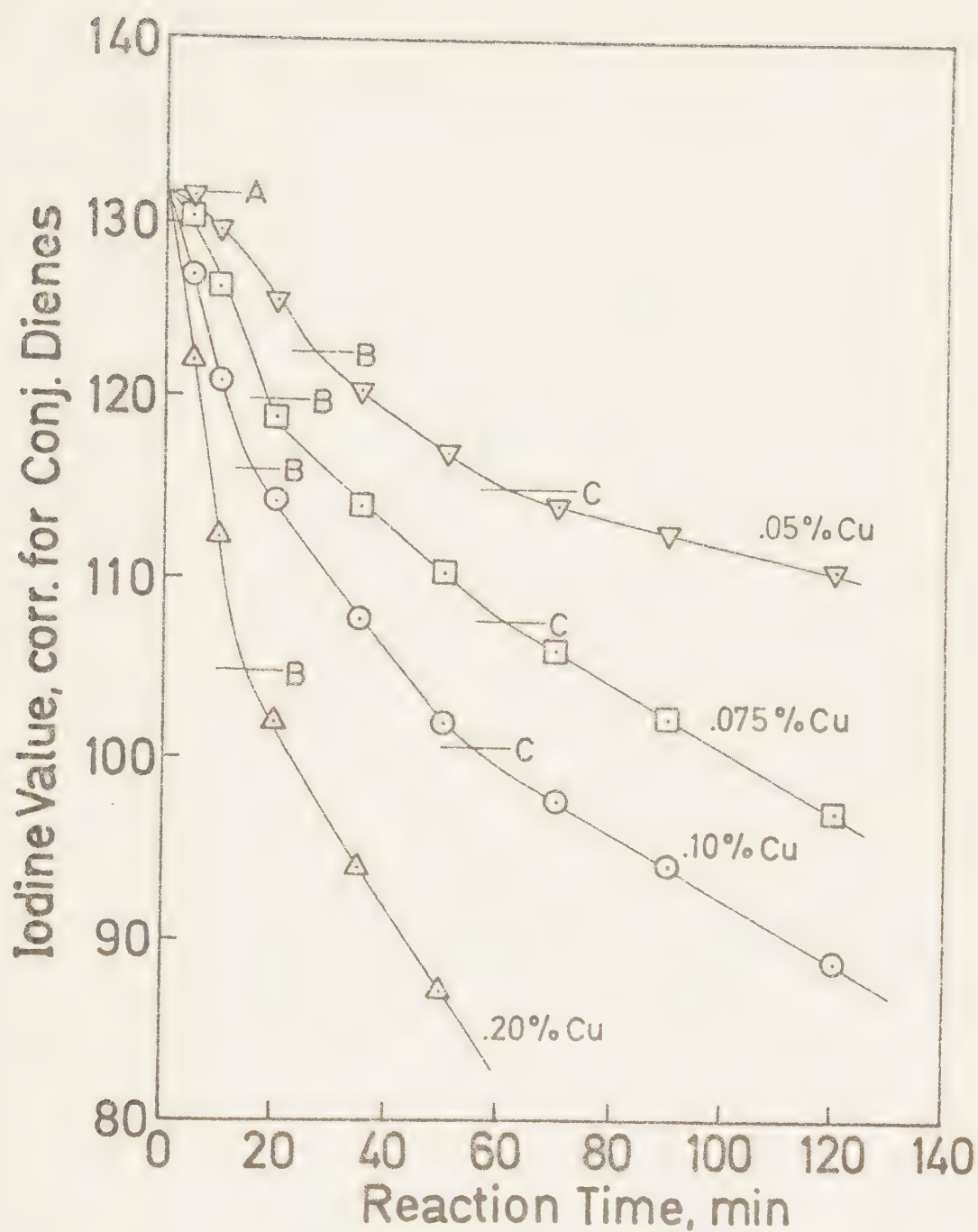


FIG. 2. Effect of catalyst concentration in soybean oil hydrogenation (Cu-1106P catalyst, 6 atm and 185 C).

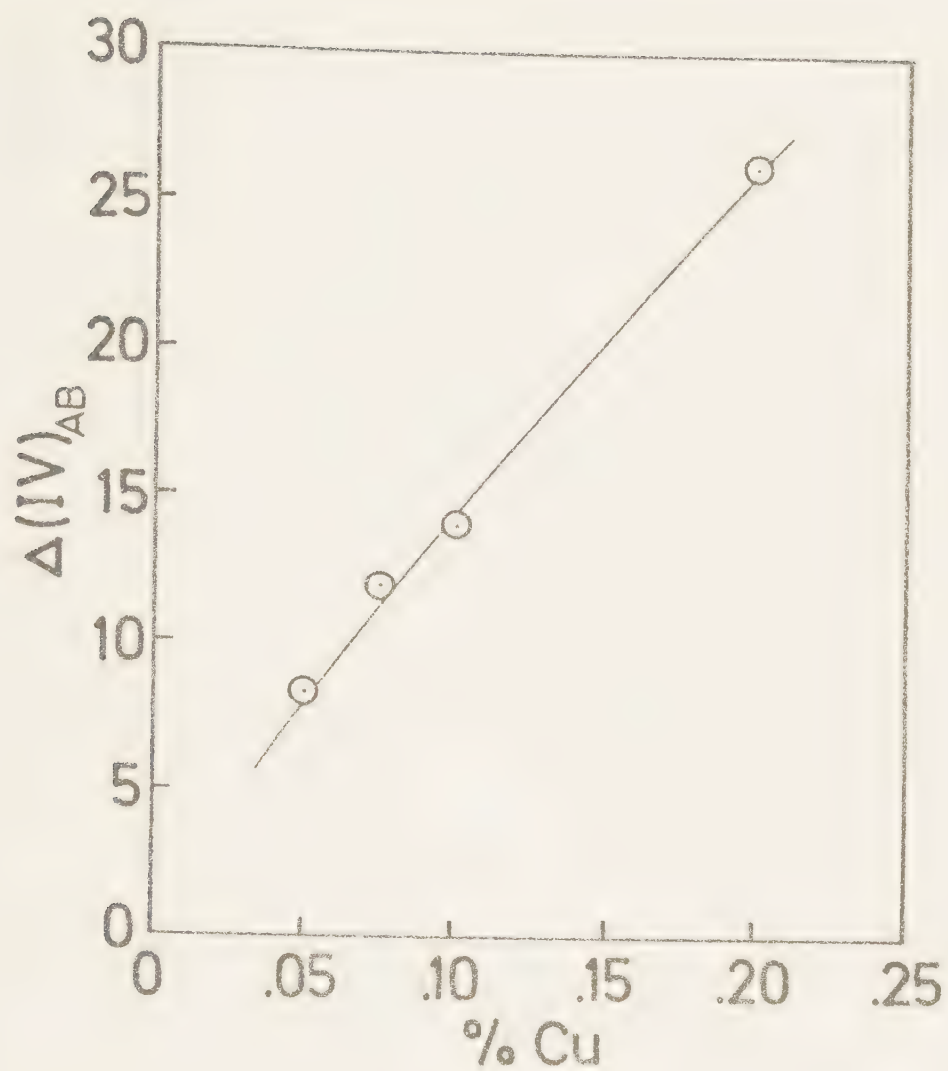


FIG. 3. Hydrogenation of soybean oil with the Cu-1106P catalyst at 6 atm and 185 C: $\Delta(IV)_{AB}$ versus catalyst concentration.

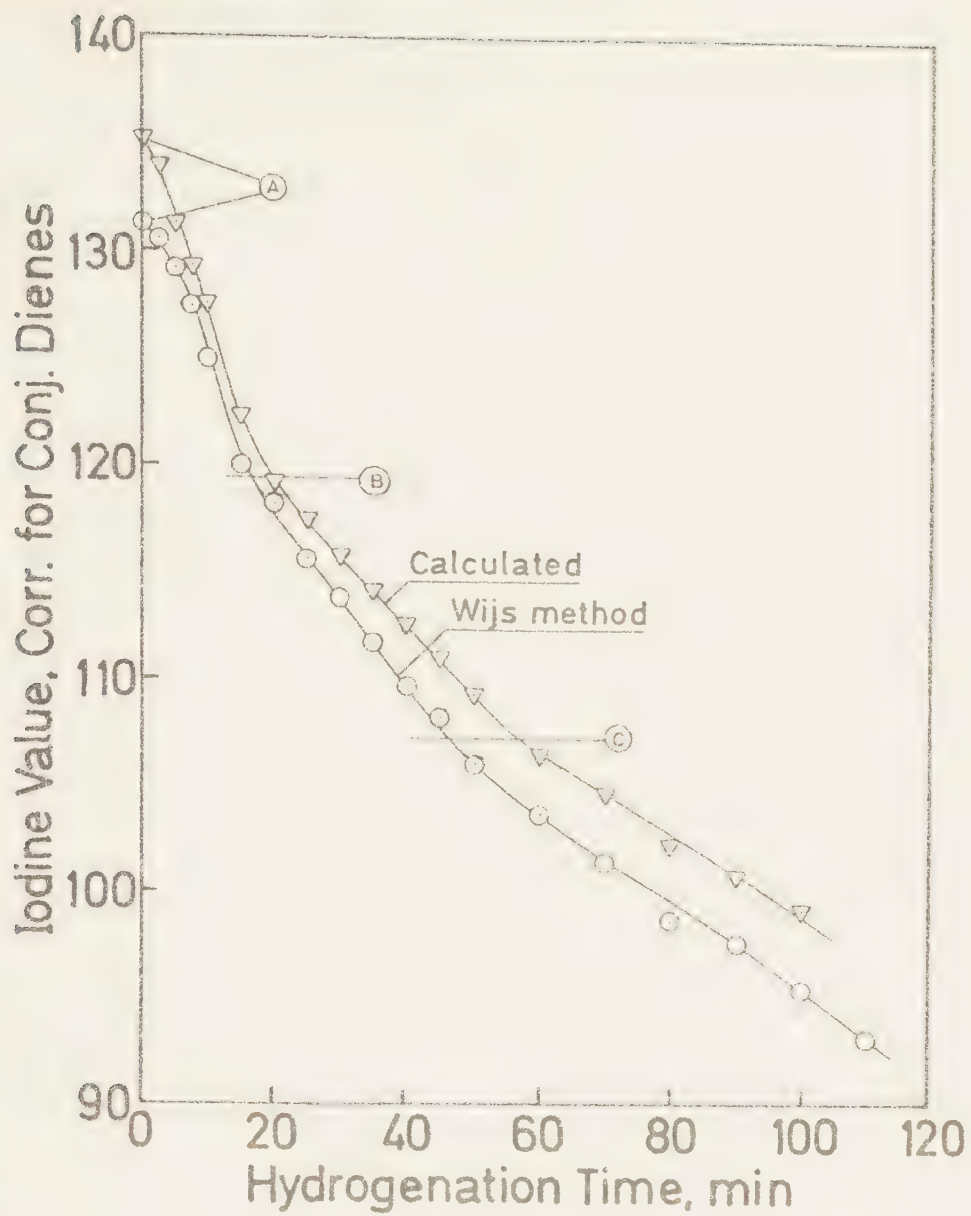


FIG. 4. Iodine value versus reaction time in the hydrogenation of soybean oil (Cu-1106P, 0.1 wt-% Cu in the oil, 3 atm, and 185 C).

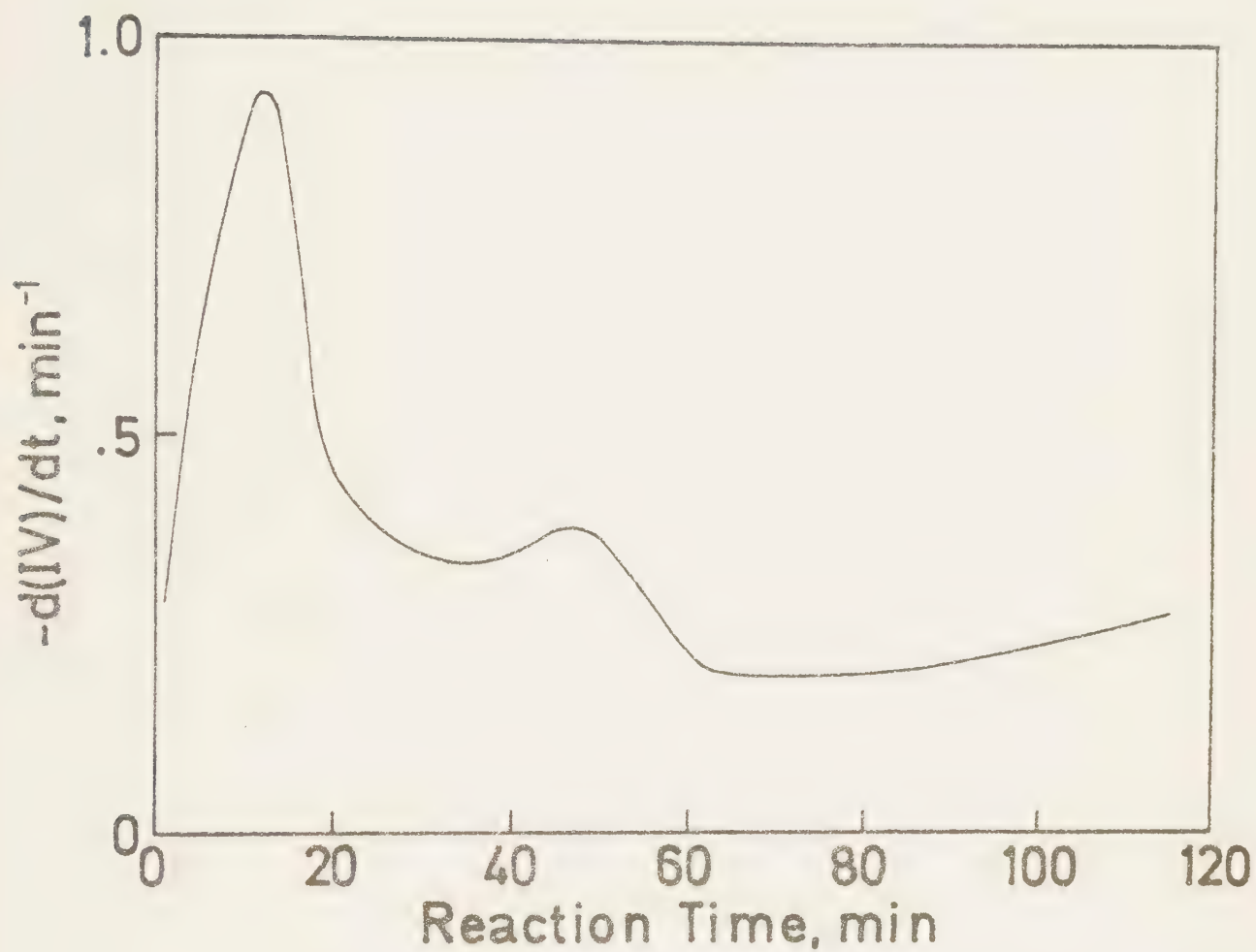


FIG. 5. Hydrogenation rate $-d(IV)/dt$ versus the reaction time of the hydrogenation run in Fig. 4 (from the IV graph according to the Wijs method).

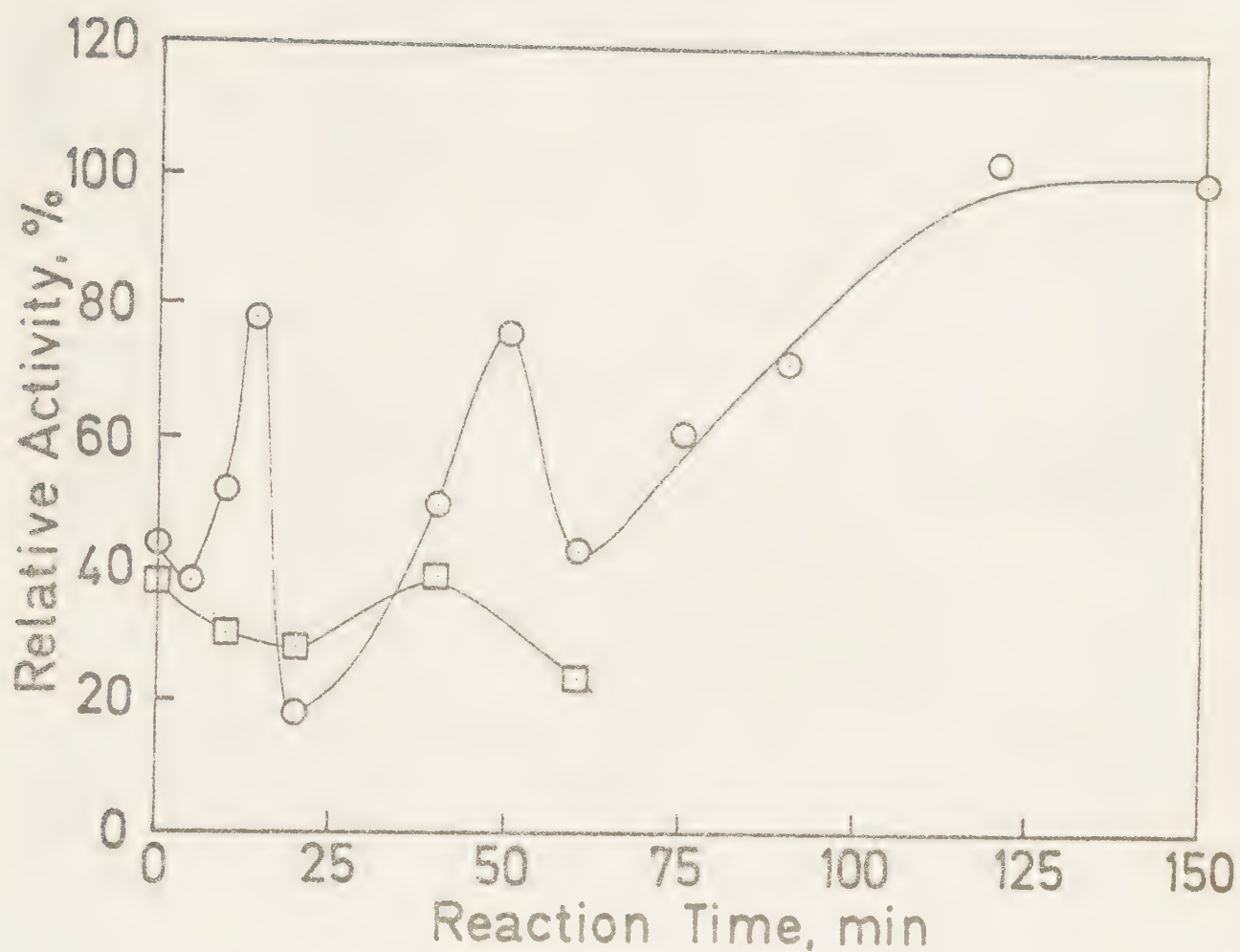


FIG. 6. Relative activity of the Cu-1106P catalyst according to the direct measurements after its use in soybean oil at 3 atm/185 C (Δ) and in rapeseed oil at 6 atm/185 C ($\square$); 0.10 wt-% Cu in the oil. $y = 3.0$.

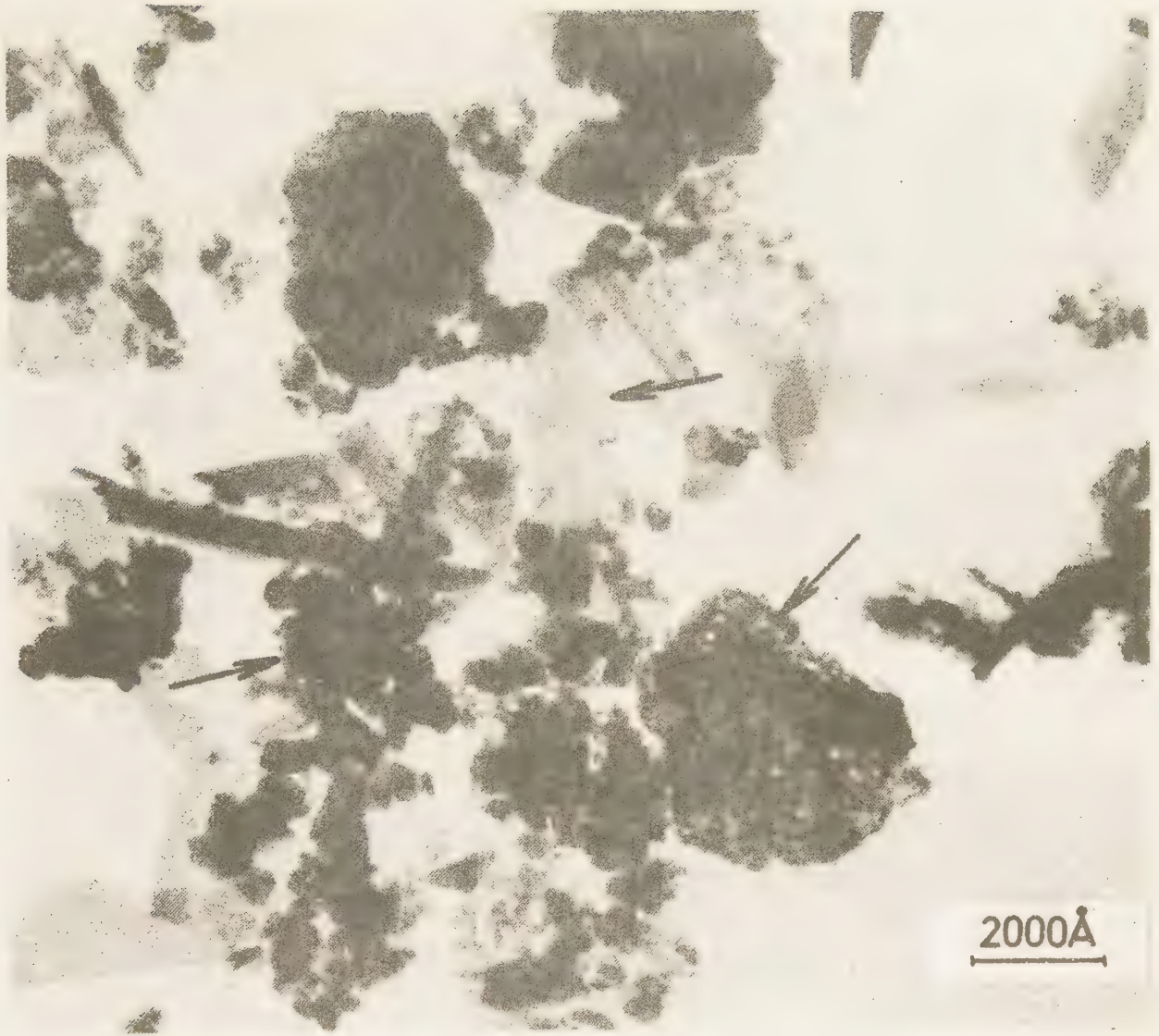


FIG. 7. Cu-1800P catalyst on carbon film.

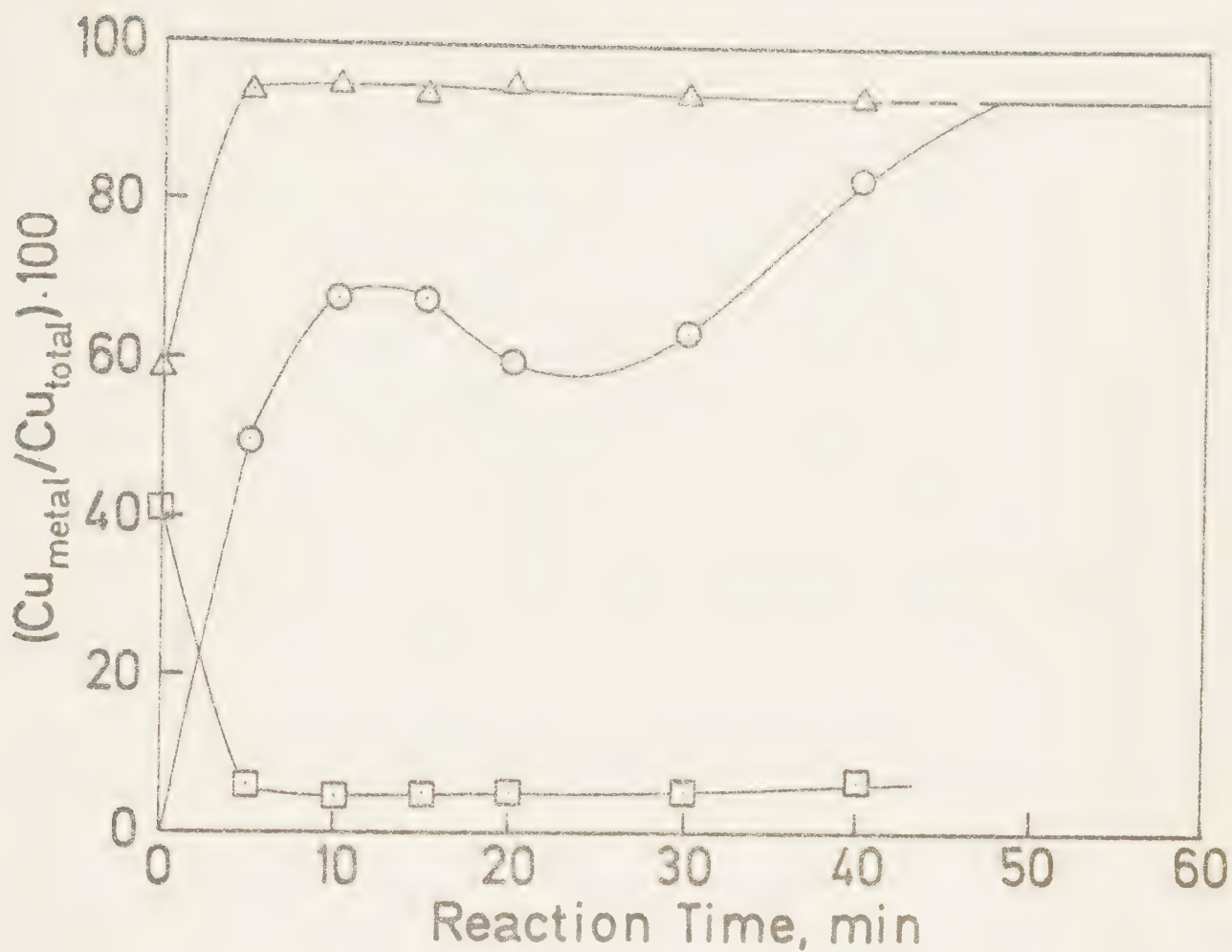


FIG. 8. Changes of the phase composition from the X-ray diffraction analyses (O) and from the solubility data (HCl fraction Δ and $\text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$ fraction $\square$); Cu-1106P, 0.1 wt-% Cu in soybean oil, 3 atm, and 185 C.

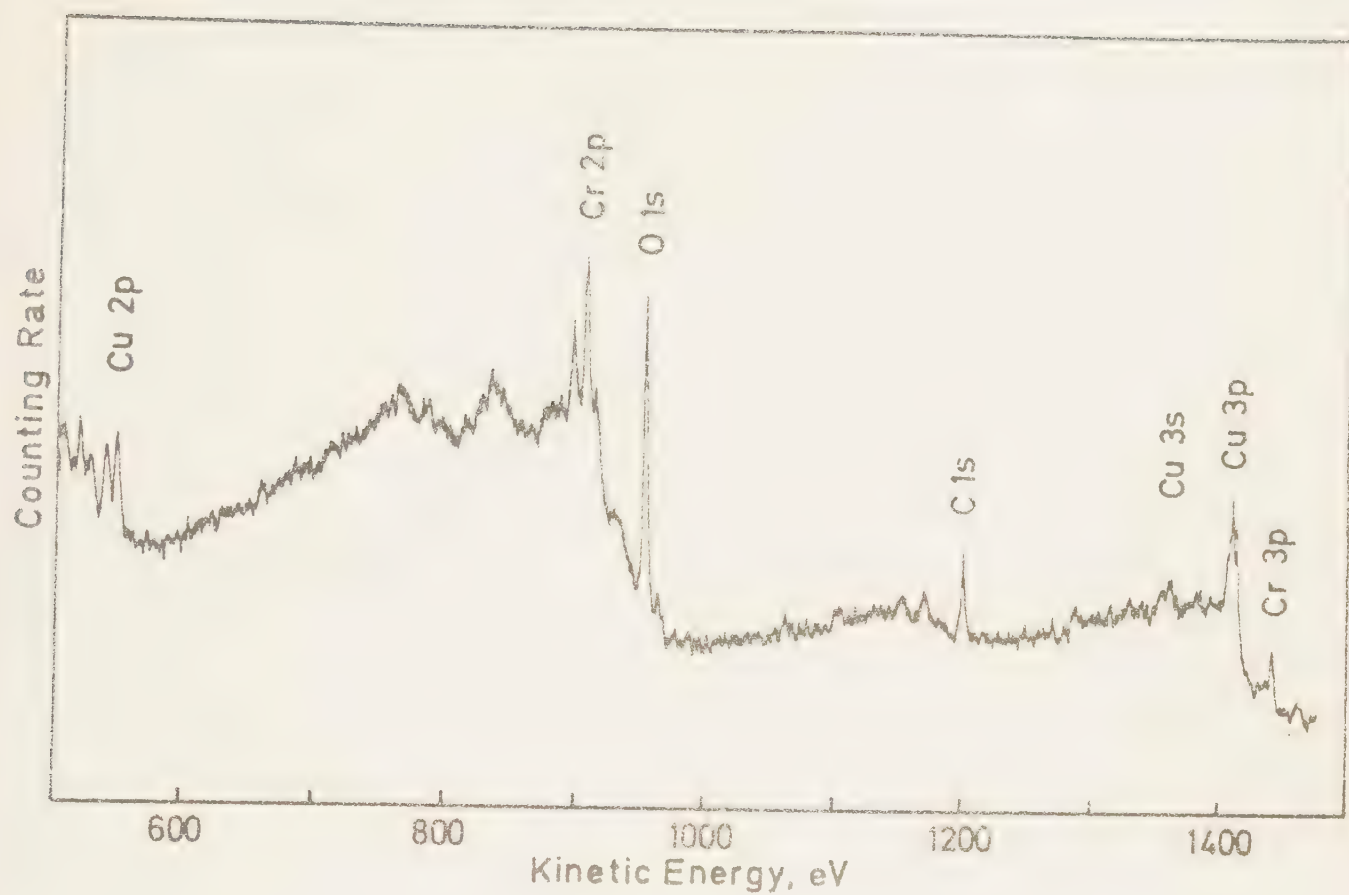


FIG. 9. A wide scan ESCA spectrum of the original Cu-1800P catalyst at 25 C.

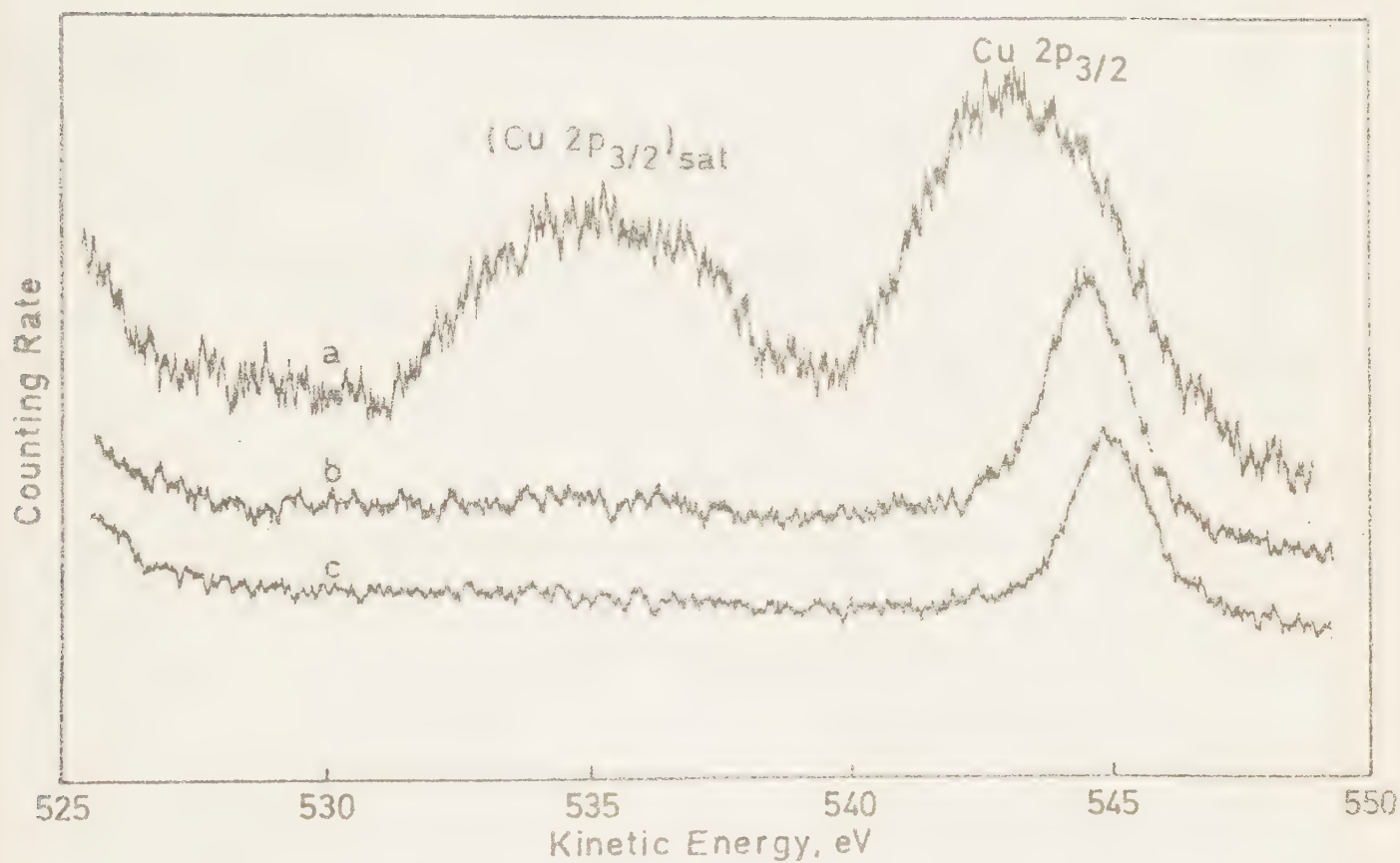


FIG. 10. The Cu2p_{3/2} peak with the adjacent satellite peak of the ESCA spectrum of (a) the original Cu-1800P catalyst, the catalyst used for (b) 5 minutes and (c) 50 minutes in a soybean oil hydrogenation at 3 atm and 185 C.

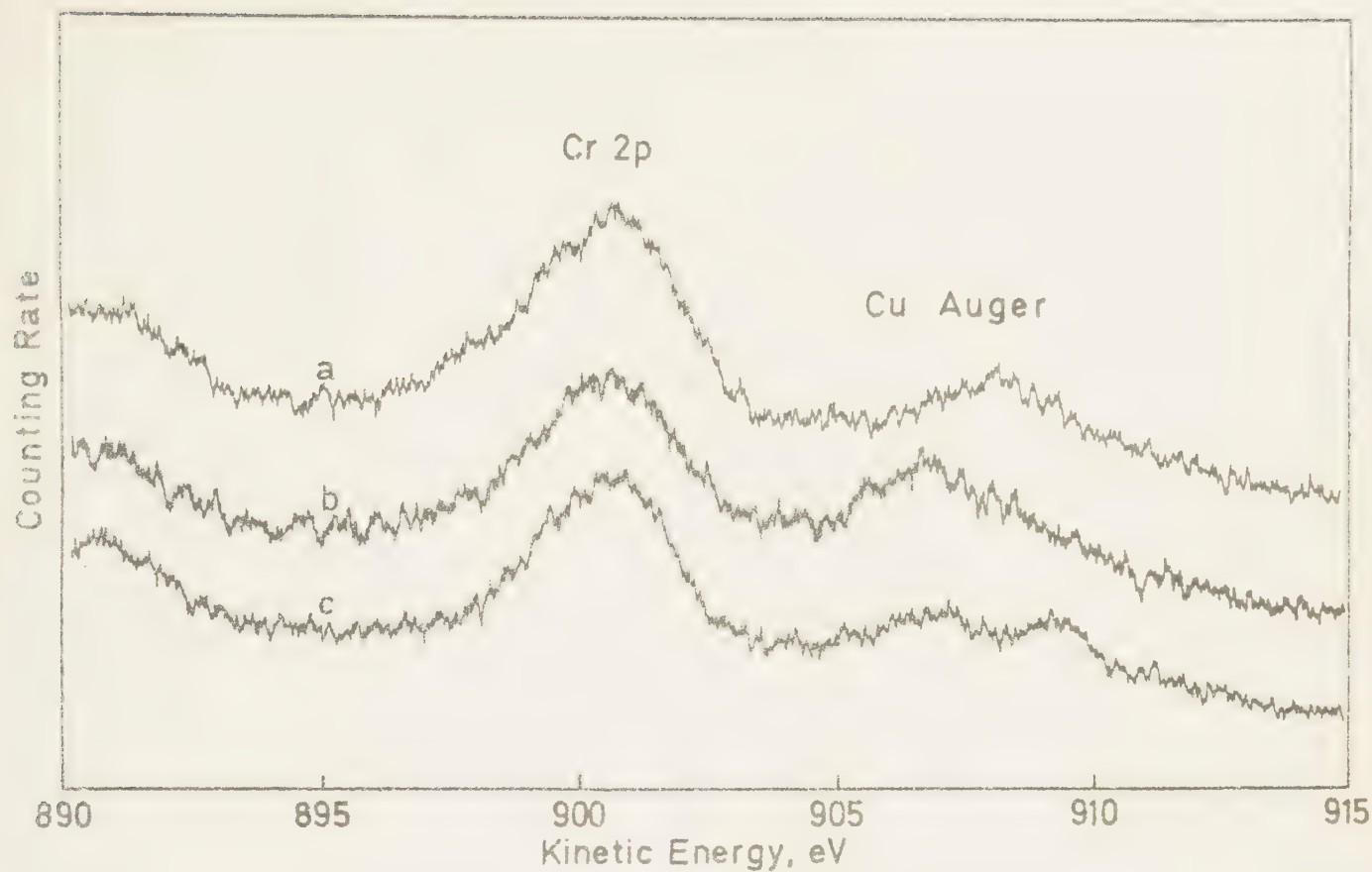


FIG. 11. The Auger electron spectra of the Cu-1800P catalyst:
(a) original catalyst, (b) catalyst used for 5 minutes, and
(c) 50 minutes in a soybean oil hydrogenation at 3 atm and 185 C.

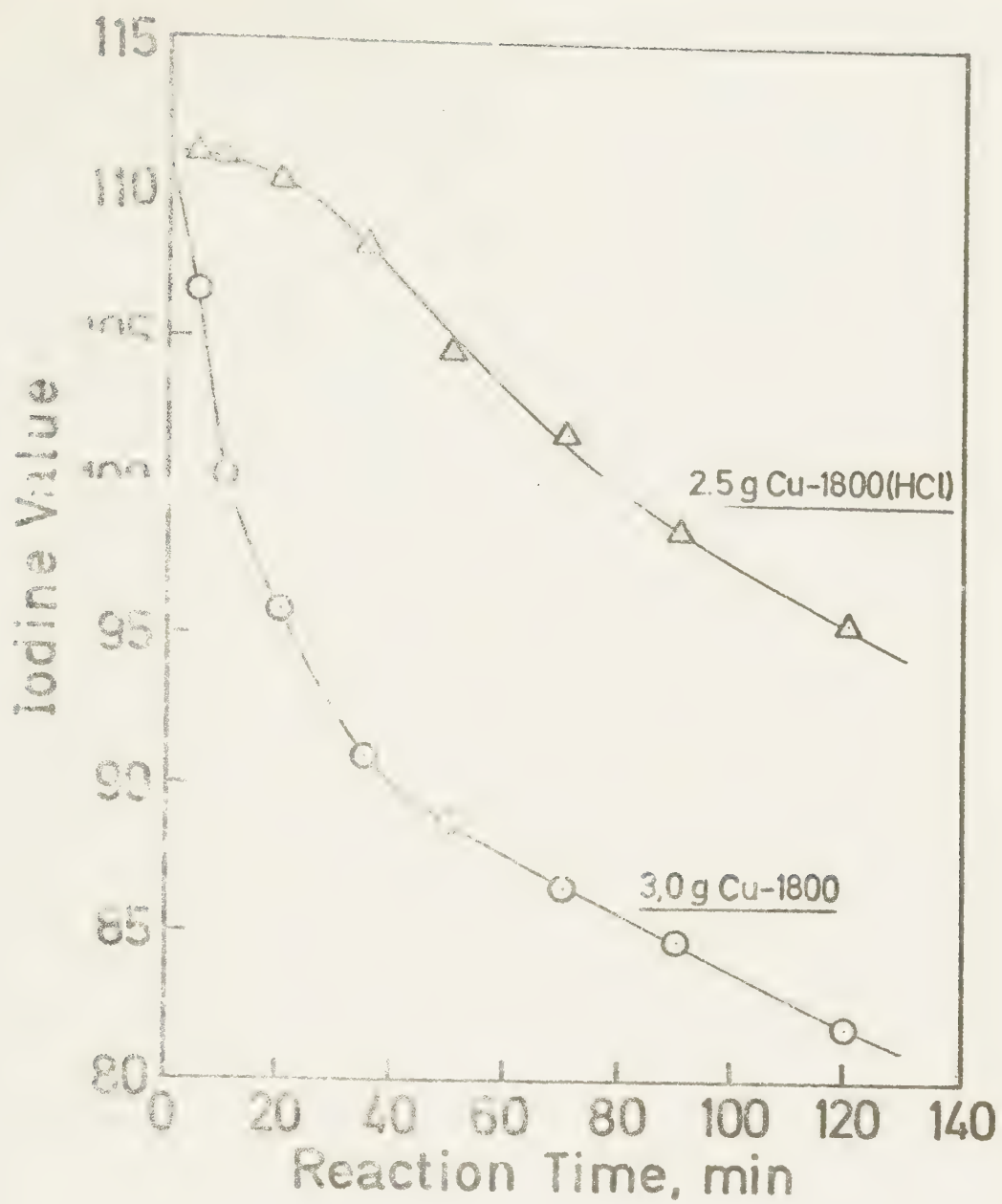


FIG. 12. A comparison between original and HCl-washed Cu-1800P catalyst (rapeseed oil, 6 atm, and 185 C).

COPPER CATALYSTS IN THE SELECTIVE HYDROGENATION OF SOYBEAN
AND RAPESEED OILS: II. THE EFFECT OF A HYDROGEN FLOW OVER
COPPER CHROMITE CATALYST

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Copper Catalysts in Selective Hydrogenation of Vegetable Oils.

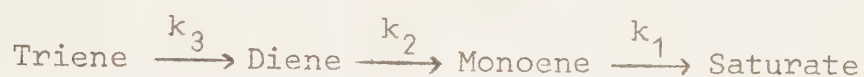
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ABSTRACT

The time required for a hydrogenation of soybean and rapeseed oils to a linolenate content of 1-2% with a copper chromite catalyst is reduced to 40-60% if the dead-end system is replaced with a procedure using a flow of hydrogen through the reactor. The effect is to be ascribed to the removal of oxidation products, acting as catalyst poisons, and the water which is formed during the reduction of the catalyst. The selectivity towards the linolenate compound is nearly unchanged.

INTRODUCTION

The advantages of hydrogenating soybean and rapeseed oils with a catalyst based on copper are the high selectivity towards the linolenic compound (S_{Ln}) and the non-existing formation of saturates (1,2). The low activity of the copper catalysts is well-known. A typical S_{Ln} value of an industrial-use nickel catalyst is 2-3 and its activity corresponds to more than 200 liter H_2 (STP)/hr·g Ni. The corresponding values of a typical copper-containing catalyst are 7-12 resp. 40 liter H_2 /hr·g Cu (3). The S_{Ln} values are then calculated as the ratio k_3/k_2 in the consecutive reaction scheme:



Most of the copper-containing catalysts are composed of copper in its divalent state. The copper is partially reduced to metal during the hydrogenation.

When the copper of a hydrogenation run with 0.1 wt-% Cu in the oil is reduced to Cu metal, water is generated in an amount which corresponds to ca. 300 ppm water. The addition of 400 ppm water to a specially refined soybean oil reduces the rate of hydrogenation in a dead-end system to 70% (4). In the dead-end system, the reactor is supplied with as much hydrogen as the oil consumes and dispersion of the hydrogenation gas is assisted by mechanical agitation. The water formed remains within the autoclave.

Konetzke et al. (5) reported the deactivating effect of water on the hydrogenation of fatty acids with copper chromite

catalysts. Miya et al. (6) made use of a copper chromite catalyst in the hydrogenation of fatty esters to higher alcohols. They studied the adsorption of water on a reduced catalyst at the pressure of 10 kp/cm^2 . Water was adsorbed until equilibrium was reached on the catalyst surface. The adsorption resulted in the deactivation of the catalyst.

The poisoning effect in connection with the adsorption of water on the surface of reduced copper is thoroughly discussed in literature. However, the copper chromite catalyst has high activity also during the two periods of catalyst reduction (5), when water is being generated. In the fat hydrogenation process the effect of water is thus of special interest.

During reduction, the surface layer of the copper chromite catalyst consists of a mixture of copper metal atoms and oxidic copper. Hydrogen spillover is quite possible between the metal atoms and the oxide at such a surface. Water has been found to enhance the conditions for dissociative adsorption of hydrogen in systems in which the hydrogen spillover is assumed to occur. Boudart et al. (8) reported that yellow tungsten(VI)oxide, catalyzed by platinum black at room temperature, can be reduced by molecular hydrogen to form blue solids with a molar composition of $\text{H}_{0.35}\text{WO}_3$, if water was pre-adsorbed at the surface of the WO_3 . They reported similar results in the reduction of copper(II)oxide, though the CuO experiments were difficult to evaluate due to the fact that the reduction generated water. The co-catalyst water acts as a proton acceptor and the transported species are the solvated protons (9).

We have found that the time which is required to reduce the linolenate content of the soybean oil to ca.

1% may be reduced if the dead-end system is replaced with a procedure combining the mechanical agitation of the dead-end autoclave with a limited flow of hydrogen through the oil. The resulting procedure is called "flow procedure". The results from a hydrogenation using flow procedures have been published earlier by others (10,11), however, without discussing the implications.

A flow of hydrogen gas through the oil and out from the autoclave may affect the conditions of hydrogenation by a) improving phase contact gas/liquid, b) maintaining the hydrogen pressure in the headspace, and c) removing water and other catalyst poisons. These three effects and their consequences have been studied here. The dead-end procedure has been compared to flow procedures. Data in the comparison is given on the basis of the time required for an iodine value drop of 15 units, after which the content of linolenic acid ester normally is reduced to about 1% in soybean oils and 1-2% in rapeseed oils.

EXPERIMENTAL PROCEDURES

Material

Commercially refined and bleached soybean and rapeseed oils were hydrogenated. The percentage of erucic acid in the different rapeseed oils was ca. 17%.

The Cu-1106P catalyst was supplied from Harshaw Chemical Company (40% CuO, 47% Cr₂O₃, and 10% BaO). In the experiments for the mass spectrometric analyses, a hydrogen gas of high purity was used, (99.99%; 5 vpM H₂O, 3 vpM O₂, and 100 vpM N₂).

Analytical Methods

Most of the analytical methods used have been previously described (7). Methyl esters, prepared from oil samples with sodium methylate catalyst and dimethyl carbonate, were analyzed with a 9 ft. x 1/8 in. stainless steel column packed with 7% BDS on 80/100 Chrom W and a flame ionization detector. Iodine values were determined according to the Wijs method. The percentage of conjugated dienes was calculated from the UV absorption at 232 nm. The amount of crystalline copper metal in the catalyst samples was determined from X-ray diffraction analysis with the barium chromate phase as an internal standard.

The percentage of isolated trans was estimated by IR absorption in carbon disulphide with methyl elaidate as the standard.

The mass spectroscopic analysis of the gas streams was carried out with the mass spectrometer AEI MS 10 with a continuous inlet system. The gas to be analysed was introduced through a heated capillary. The pressure of the analyser tube was $2 \cdot 10^{-6}$ Torr and a scan from m/e 12 to m/e 45 or from m/e 36 to m/e 200 was performed in 11 minutes.

The amount of water in the gas was estimated on the basis of the ratio between the peaks at m/e 17 and m/e 15. The signal m/e 17 represented water with the relative intensity of 23% (m/e 18 = 100%).

Equipment and Operating Procedures

The hydrogenation procedure in the 1 liter Parr apparatus was described earlier (7). In the normal procedure, 300 g oil was hydrogenated at a stirrer rate of 1 700 rpm and at a temperature of 185 C. The hydrogen flow through the oil was measured after passing through the outlet valve at 1 atm and 20 C. No hydrogen was recirculated.

RESULTS AND DISCUSSION

The Transfer of Hydrogen

In order to enable a direct observation of the stirrer function, a copy of the reactor cylinder was made of transparent material. The stirrer was rotated and a flow of hydrogen was led through the oil at room temperature and atmospheric pressure. The amount of oil was varied at two levels, 300 and 600 g.

Cooling coils, stirrer-bearer, and sampling tube caused vigorous turbulence within the oil phase. At 700 rpm, the entire oil bulk was filled with bubbles, 0.5 - 2 mm in diameter. At 1700 rpm, the oil was thrown into the headspace and the enclosed gas was effectively changed. The contact between the oil and gas phases was more effective with 300 g at 1700 rpm than with 600 g at 700 rpm, but, under no circumstances did a flow of 50 liter H_2 /hr influence the picture of bubbles in the oil bulk.

In the dead-end hydrogenations, the rate of hydrogenation was found to be independent of the stirrer rate in the interval

700 - 1700 rpm. A further increase of the interface gas/liquid caused by a hydrogen flow of 50 liter/hr through the oil did not improve the conditions of mass transfer in the processing of 300 g oil at 1700 rpm.

An estimation of the resistances of external hydrogen transfer has been performed on the basis of the film model. In that model, the resistances were fixed to the liquid films near the gas bubbles and near the catalyst particles. These two films were both affected by the stirrer rate. A flow of hydrogen may affect the size of the interfacial area gas/liquid.

The hydrogen transfer of the film gas/oil has been studied according to the procedure described by Pihl and Schöön (12). As the interfacial area gas/oil is difficult to determine, the rate of mass transfer is calculated per unit volume of dispersion. The product of the mass transport coefficient in the liquid film near the gas bubbles k_L and the specific interfacial area a is called the volumetric mass transfer coefficient $k_L a$ and the mass transfer equation of the interface gas/oil may be written:

$$N = k_L a (c_0 - c) \quad [1]$$

where N = rate of hydrogen transfer, mole H_2 (sec·l oil)⁻¹,
 k_L = mass transfer coefficient in the liquid film near the bubbles, cm·sec⁻¹, c_0 = hydrogen concentration in the gas-oil interface, is equal to the solubility of hydrogen, mol (l oil)⁻¹ and
 c = hydrogen concentration of the bulk, mole (l oil)⁻¹.

At sufficiently high catalyst loadings, the value of c may be neglected due to a high rate of reaction. If $1/N$ is plotted versus $1/m$, where m is the catalyst loading, the $k_L a$ value is obtained from the intercept at the ordinate axis. The extrapolation is facilitated if $1/N$ is plotted versus $(N^{1-b}/m)^{1/b}$ where $b = 1.1$ for the nickel catalyst (12).

The $k_L a$ -value of the autoclave was determined during the conditions of a typical copper hydrogenation: 185 C, 2 atm, 300 g soybean oil, 1700 rpm, and 50 liter H_2 /hr. However a pre-reduced nickel catalyst G-53 was used to avoid the reduction stages of the copper catalyst. The volumetric mass transfer coefficient $k_L a$ was found to be 0.65 sec^{-1} .

The mass transfer coefficient k_H for the transport of hydrogen from the oil bulk to the external surface of the catalyst particles had been estimated on the basis of the results of Levins and Glastonbury (13) according to the calculation procedure given by Bern et al. (14). The mean particle size of the Cu-1106P catalyst used was determined as $2.2 \cdot 10^{-3} \text{ cm}$ (15). The power number N_p of the impeller was estimated as 2 (13) resulting in a specific power group 0.96. The coefficient k_H was estimated as $0.42 \text{ cm} \cdot \text{sec}^{-1}$.

The concentration differences Δc over the two films have been calculated from the equations:

$$N = 0.65 (\Delta c)_1 \quad [2]$$

$$N = 0.42 \cdot a_p \cdot (\Delta c)_2 \quad [3]$$

where Δc = concentration differences over the film near the bubbles [2] and near the catalyst surface [3], mole (l oil) $^{-1}$

and a_p = external surface of the spherical particles per volume of oil, cm^{-1} .

The concentration differences were calculated for a series of Cu-1106P hydrogenations (Table I). The value of N which was used was the maximal rate of reaction $-d(\text{IV})/dt$ of each run. The maximal concentration difference of the film near the gas bubbles was less than 6% of the hydrogen solubility. The concentration difference of the film between the oil and the catalyst particle was negligible.

The Dilution Effect of the Reduction Water

If the copper in the copper-containing catalyst, which is supplied to the oil in its divalent state, is completely reduced, 0.16 mole of water is generated per kg oil and the percentage unit Cu in the oil (wt-%). Provided that all the water formed is transferred to the gaseous phase, the maximum hydrogen dilution due to the reduction of the catalyst may be estimated from the expression

$$-\Delta p_{\text{H}_2} = p_{\text{H}_2\text{O}} = C_{\text{Cu}} \frac{m_{\text{oil}}}{V_{\text{hs}}} \cdot 0.16 RT \quad [4]$$

where $-\Delta p_{\text{H}_2}$ = decrease of the hydrogen pressure, atm,
 $p_{\text{H}_2\text{O}}$ = partial pressure of water, atm, C_{Cu} = wt-% Cu in the oil,
 m_{oil} = amount of oil in the autoclave, kg, V_{hs} = volume of the headspace, liter, $R = 0.082 \text{ liter atm mole}^{-1} \text{K}^{-1}$, and
 T = temperature, K.

The effect of hydrogen pressure on the rate of hydrogenation will be discussed in the following paper. Here an approximate correlation is sufficient between the time required for an

iodine value drop of 15 units, t_{15} min, and the hydrogen pressure P_{H_2} atm (approx. equal to the total pressure P atm at flow hydrogenations). For pressures between 2 and 6 atm the time t_{15} can be written:

$$t_{15} = t_{15}^* + \frac{t_{15}}{4} (6 - P) \quad [5]$$

where the time t_{15}^* is determined from a hydrogenation run at the pressure 6 atm with C_{Cu} wt-% Cu in the oil. The maximum effect of hydrogen dilution due to the reduction water is obtained from equations 4 and 5 :

$$\Delta t_{15} = t_{15} - t_{15}^* = \frac{t_{15}^*}{4} \cdot (-\Delta P_{H_2}) \quad [6]$$

$$\Delta t_{15} = C_{Cu} \cdot \frac{t_{15}^*}{4} \cdot \frac{m_{oil}}{V_{hs}} \cdot 0.16 RT \quad [7]$$

In a typical hydrogenation run in the Parr apparatus ($C_{Cu} = 0.1$ wt-%, $t_{15}^* = 30$ min, $m_{oil} = 0.3$ kg, $V_{hs} = 0.57$ liter, and $T = 458$ K) the prolonging effect of hydrogen dilution at dead-end hydrogenation is in the order-of-magnitude of 2 minutes, i.e. within the margin of errors. However, with 0.6 kg oil in the bomb ($m_{oil}/V_{hs} = 3$) the increase of reaction time is about 13 minutes.

Mass Spectrometric Analyses of the Gas Stream

The volatile substances, which leave the oil with the hydrogen flow, exist either in the bleached oil or are generated during the process. The mass spectrometric analyses of the gas stream from the autoclave were performed during the rapeseed oil hydrogenation, because these oils normally contain more catalyst poisons than soybean oils. Water vapour and carbon compounds with up to six or seven carbon atoms were detected. The spectra

obtained have not been studied in detail. No other compound was found with the possible exception being substances concealed within the groups of signals representing the carbon chain fragments. Especially, no hydrogen sulphide was detected. In that respect, the result was confirmed by leading the outlet gas of several hydrogenation runs through a zinc acetate solution, which was analysed according to the procedure described by Gustafson (16).

The MS analyses of the outlet gas flow from the autoclave during flow hydrogenations included the estimation of the water content of the gas. The reduction water leaves the oil in two periods, reflecting the two periods of catalyst reduction (Fig. 1). The maximum partial pressure of water in the headspace during a run at 6 atm with 2 g of Cu-1106P catalyst is about 140 Torr (0.19 atm) and the mean value of the second period of catalyst reduction and water removal corresponds to about 15 Torr.

The Organic Compounds of the Hydrogen Stream

The organic compounds, leaving the autoclave with the hydrogen flow, were isolated as follows: 300 g of soybean oil were purified from volatile substances in two steps. To remove air oxygen and other dissolved gases the oil was heated at 90 C and 1-2 Torr for 40 minutes. In the second step, the oil was stirred at 185 C while continuously flushing it under reduced pressure (20-40 Torr and ca. 10 liter N_2 /hr) which contained less than 10 vpm O_2 . 1 g of Cu-1106P catalyst was added and the oil was hydrogenated at 185 C and 6 atm H_2 pressure according to the normal procedure which included a heating-up period.

The flow of gas leaving the oil during the two purification steps, the heating-up period prior to the hydrogenation, and the hydrogenation was led through a cold-trap with liquid nitrogen. The four condensates, with the exception of the oil drops situated in the head of the cold-traps, were dissolved in iso-octane (spectro grade). The solutions, giving off a strong odor, were subjected to UV absorption analysis (Fig. 2).

The spectrum of the first condensate shows two distinct maxima, indicating the presence of a conjugated compound. Conjugated dienes, trienes, and tetraenes, in the full sense of the concepts, were leaving the oil during the N_2 stripping. The spectrum obtained from these condensates may be ascribed to oxidation products formed during the bleaching process (17). Such compounds were present in the oil (Fig. 3) and normally, when no nitrogen stripping at 185 C occurred, these compounds were found in the hydrogen flow leaving the autoclave. With nitrogen stripping, the UV absorption spectrum from the hydrogenation step did not show the clear maxima from the conjugated trienes, but rather the dienes dominated. On the whole, the condensate shows a smaller absorption of the conjugated dienes and trienes in comparison to the peak at 220 nm.

In Figure 4, the time required for an iodine value drop of 15 units for seven soybean oils was plotted versus the UV absorption at 232 nm. Obviously, the pre-conjugation had a negative effect on the rate of hydrogenation.

The poisoning effect of oxidation products was studied by the addition of 1 g of selenium dioxide (0.009 mol) to soybean

oil, together with the catalyst. Conjugation occurred, resulting in an UV absorption spectrum similar to that of the condensates during the nitrogen stripping. With exception of some initial reduction of the iodine value, the catalyst poisoning was total.

To evaluate the total poisoning effect of volatile components, including water, the condensate from a normal flow hydrogenation of rapeseed oil (1 g of Cu-1106P, 6 atm, 185 C, and 50 liter H_2 /hr) was added to 300 g easily hydrogenated soybean oil, prior to a dead-end hydrogenation. The time required for an iodine value drop of 15 units increased from 23 to 85 minutes.

The effect of nitrogen stripping on the hydrogenation of rapeseed oil is shown in Table II. The principal difference between the dead-end and the flow procedures was not affected,

The Water of the Catalyst Reduction

The water generated during the stoichiometric reduction of the divalent copper in the Cu-1106P catalyst and transferred to the headspace of the Parr autoclave, corresponds to about 0.3 atm/g cat (185 C, 300 g oil, and a gas volume of 0.57 liter). In the case of a dead-end hydrogenation, the partial pressure of water is built up gradually, while the initial stage, in many respects, is similar to that of a flow hydrogenation.

Figure 5 shows the course of copper metal formation during a dead-end hydrogenation run. The marked second period of copper formation which was found during flow hydrogenation (7), was considerably weaker than in the dead-end hydrogenation.

The inlet hydrogen gas of a flow hydrogenation with 1 g of catalyst (0.1 wt-% Cu) was saturated with water at 55 C. Thus, the partial pressure of water in the gaseous phase in the autoclave was at least 0.15 atm during the whole process, even if the process in all other respects was a typical flow hydrogenation. The total pressure was adjusted to 3.15 atm.

The addition of water to the inlet gas increased the rate of catalyst reduction (Fig. 5). The catalyst reduction proceeded in one step, apart from the reduction of a normal flow hydrogenation. Obviously, the presence of water favours the catalyst reduction which is in accordance with the results of Boudart et al. (8).

The influence of water upon the catalyst reduction can be summarized as follows: a moderate water concentration of the oil phase favours the reduction process. Too much water retards it. In a flow hydrogenation, the water formed is continuously removed from the autoclave. The rate of reduction ceases when the main part of the catalyst has been reduced to metal.

The iodine value graphs of the dead-end and the two flow hydrogenations are shown in Figure 6. The rate of reaction $-d(IV)/dt$ is high during the catalyst reduction, which is in accordance with the results presented earlier (7). When the reduction is finished (the flow experiments only), the rate of reaction is lower in the presence of water than in its absence. The fully reduced catalyst is poisoned by water.

Comparison between the Dead-End and the Flow Procedures

The effect of a hydrogen flow on the hydrogenation time t_{15} and the selectivity towards the linolenic compound is shown in Figure 7. Table III shows the compositional data of the experiments represented in the figure. Maximum effect is obtained at a hydrogen flow of 50 liter/hr, corresponding to a gas load of 155 liter H_2 (STP)/hr·kg oil. The time required for an iodine value drop of 15 units was reduced to about 40% of the time at the dead-end procedure, independent of the oil under processing.

The maximum content of conjugated dienes in the oil, during the process, is lower during a flow hydrogenation even if the product composition, in this respect, does not show any great difference. The selectivity S_{Ln} , calculated according to the program given by Butterfield and Dutton (18), decreases with increasing hydrogen flow, but the total change is small. The amount of trans isomers formed is practically independent of the hydrogen flow.

The lower S_{Ln} -values noted for rapeseed oil are consistent with the product composition reported by Jakubowski and Pezinski (10).

Conclusions

The effect of a hydrogen flow is to ascribe to the removal of oxidation products and water. The effects due to an improved interface contact gas/oil and the avoidance of hydrogen dilution are negligible under the conditions of the laboratory experiments. The oxidation products act as catalyst poisons. The influence of water on the reactions of the solid phase and the hydrogenation is more complex.

The water concentration of the oil is regulated with the help of the hydrogen flow. In small amounts, the water enhances the conditions of dissociative adsorption of hydrogen on the catalyst surface. In larger amounts, the water acts as a catalyst poison. From the practical point of view, the flow procedure means a better utilization of the copper charged.

The industrial application of the flow procedure corresponds to a system using hydrogen recirculation including a purification train, dimensioned for a water uptake of ca. 0.3 kg water/kg copper in the catalyst.

ACKNOWLEDGEMENTS

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TABLE I

Hydrogen concentration differences of the two transport films in copper chromite hydrogenations

% Cu	$N \cdot 10^3$ $\text{mol(l} \cdot \text{sec)}^{-1}$	$\frac{(\Delta c)_1}{c_O} \cdot 10^2$	$\frac{(\Delta c)_2}{c_O} \cdot 10^2$
0.050	0.208	1.2	0.6
0.075	0.510	3.0	0.9
0.100	0.655	3.9	0.9
0.200	0.988	5.8	0.7

$$c_O = 2.58 \cdot 10^{-2} \text{ mol/l at } 185 \text{ C and } 6 \text{ atm}$$

TABLE II

Effect of nitrogen stripping.

(Cu-1106P, 0.2 wt-% Cu in rapeseed oil, 6 atm, and 185 C)

Pre-treatment	Procedure	Time $\Delta(\text{IV}) = 15$ min
Normal	Dead-end	133
N ₂ -stripping, 1 hr, 40 Torr, and 185 C	Dead-end	76
Normal	Flow	71
N ₂ -stripping, 1 hr, 40 Torr, and 185 C	Flow	29

TABLE III

The effect of a hydrogen flow on the hydrogenation product.

(Cu-1106P, 0.2 wt-% Cu in the oil, 6 atm, and 185 C).

Oil	Flow l/hr	Reaction time min	IV (Wijs)	GLC Composition			trans %	Conj. dienes %	S _{Ln} ^c
				C18:0	C18:1	C18:2 ^a %			
Soybean oil	-	-	131.5	3.8	22.1	53.0	-	0.1	-
	0	35	117.0	3.8	32.6	49.9	14.2	0.6	10.3
	12	35	114.6	4.0	33.8	48.9	14.4	0.8	10.4
	24	20	116.0	3.9	32.8	49.1	14.4	0.6	10.0
	50	20	113.3	3.7	34.8	47.9	11.0	0.9	9.1
Rapeseed oil	-	-	111.4	1.1	36.0	19.6	-	0.2	-
	0	90	96.0	1.1	40.4	22.7	11.4	0.3	7.5
	10	70	95.6	1.2	41.9	22.7	11.7	0.3	8.1
	25	50	96.8	1.1	41.0	23.0	10.8	0.4	7.4
	50	50	96.7	1.1	41.0	22.6	11.4	0.4	6.7

^a Does not include conjugated dienoates.

^b Includes conjugated dienoates.

^c Calculated from the GLC compositions.

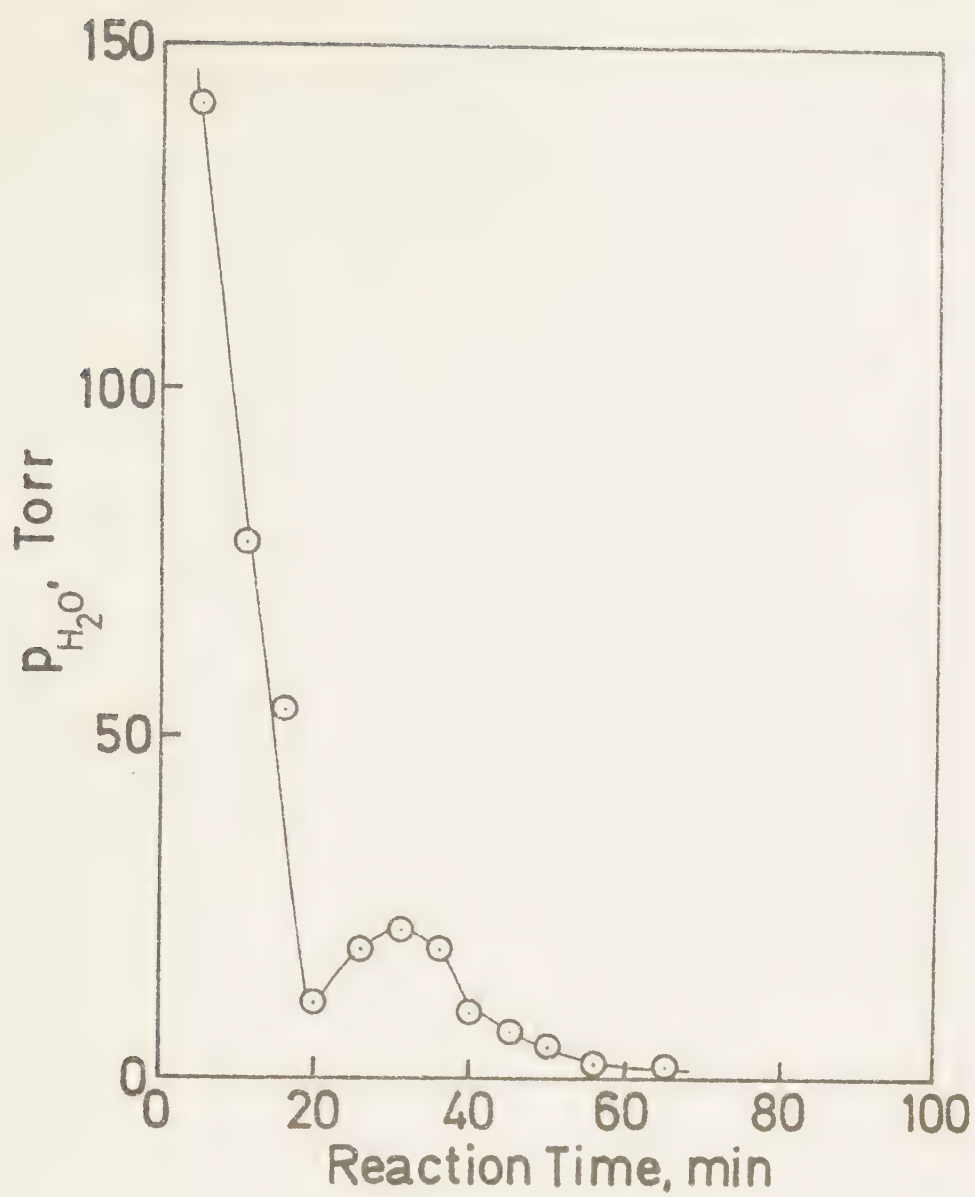


FIG. 1. Water content of the outlet flow in hydrogenation of rapeseed oil with Cu-1106P catalyst (0.2 wt-%, 6 atm, 185 C, and 50 liter H_2 /hr.

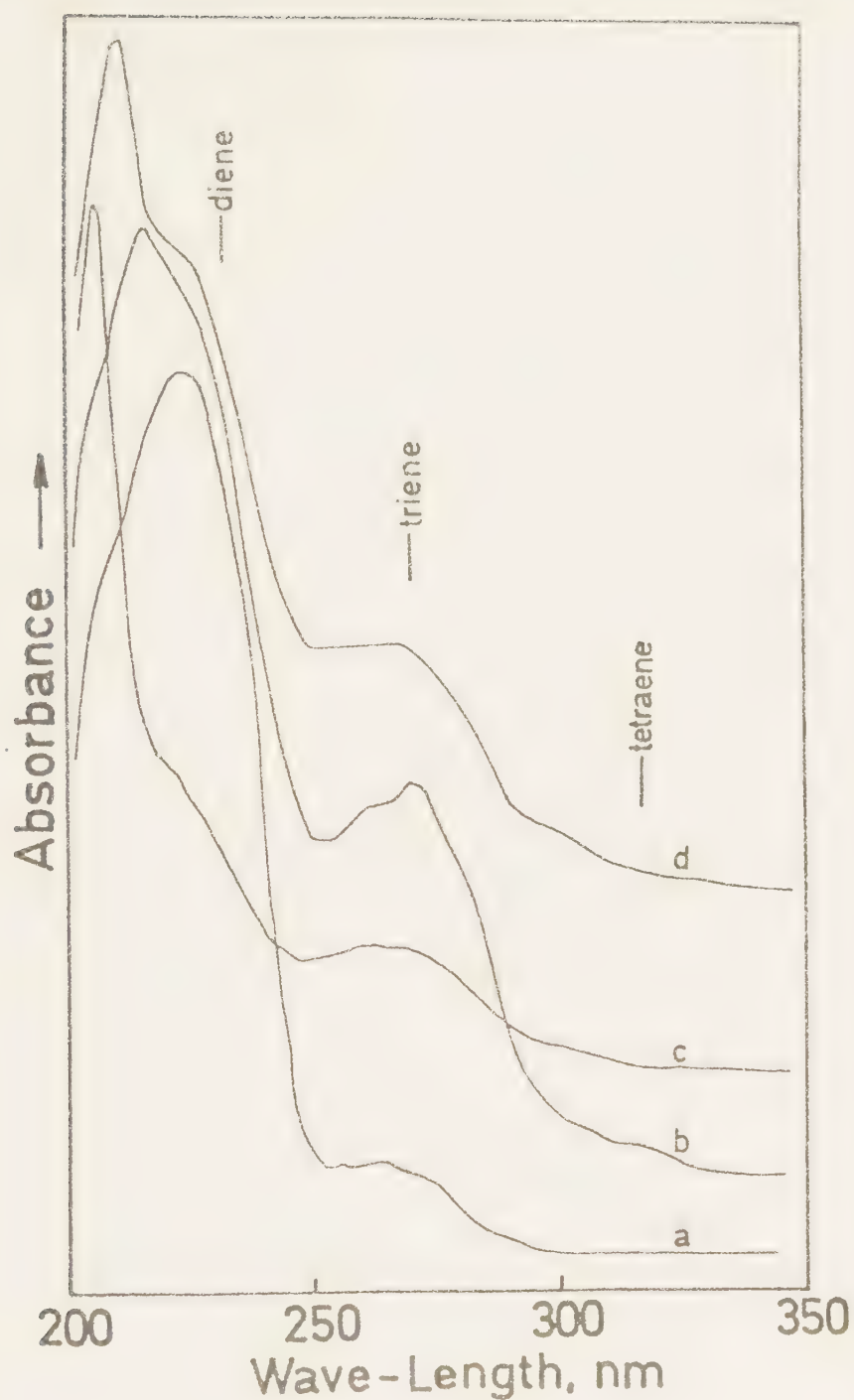


FIG. 2. UV-absorption spectra from condensates (soybean oil);
a) Degassing at 90 C and 2 Torr; b) N_2 -stripping at 185 C
and 40 Torr; c) Heating-up period; d) Hydrogenation after
degassing and N_2 -stripping (0.1 wt-% Cu, 6 atm, 185 C, and
50 liter H_2 /hr).

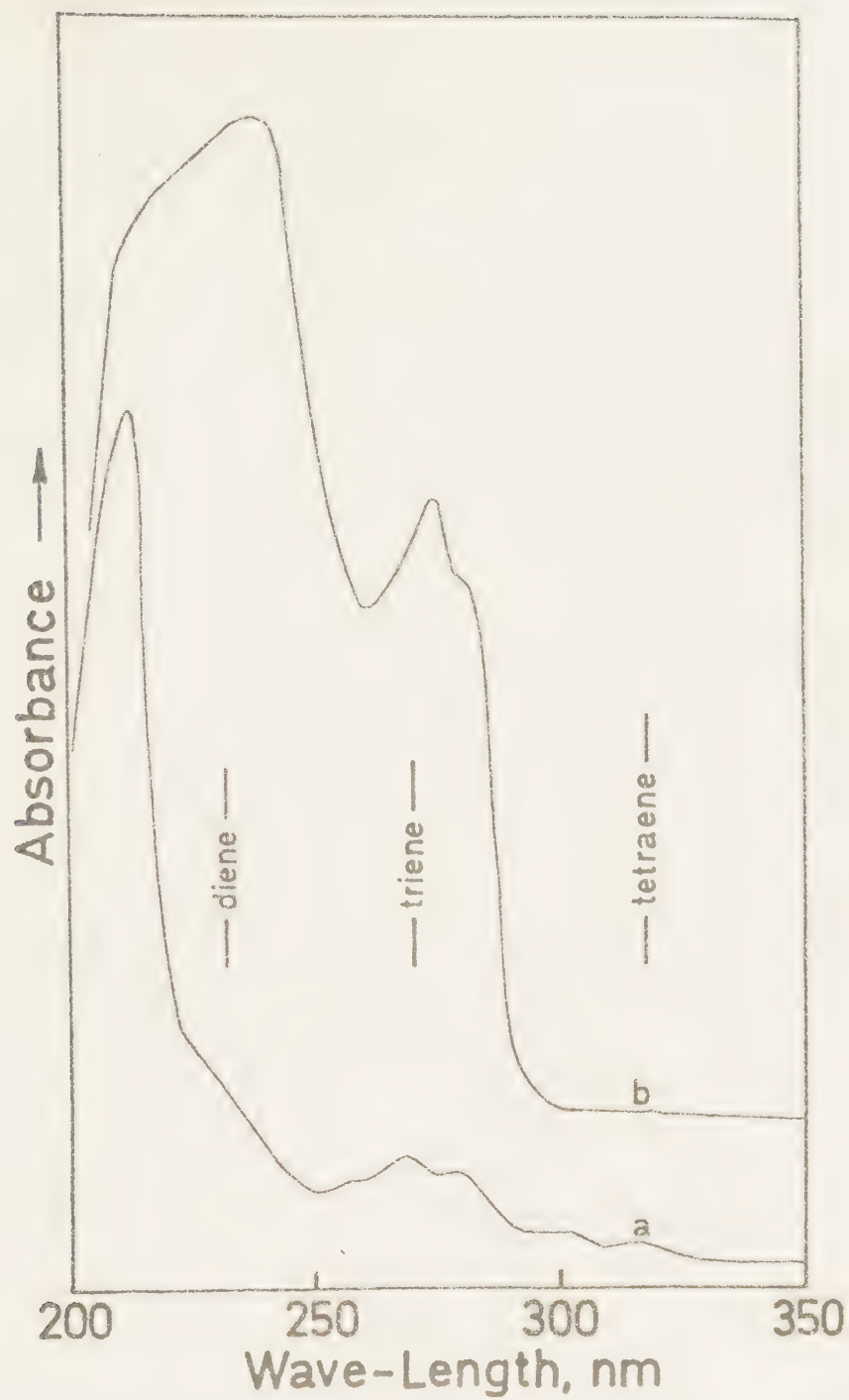


FIG. 3. UV-absorption spectra from a) original technically refined soybean oil and b) the condensate from a hydrogenation run without special pre-treatment of the oil.

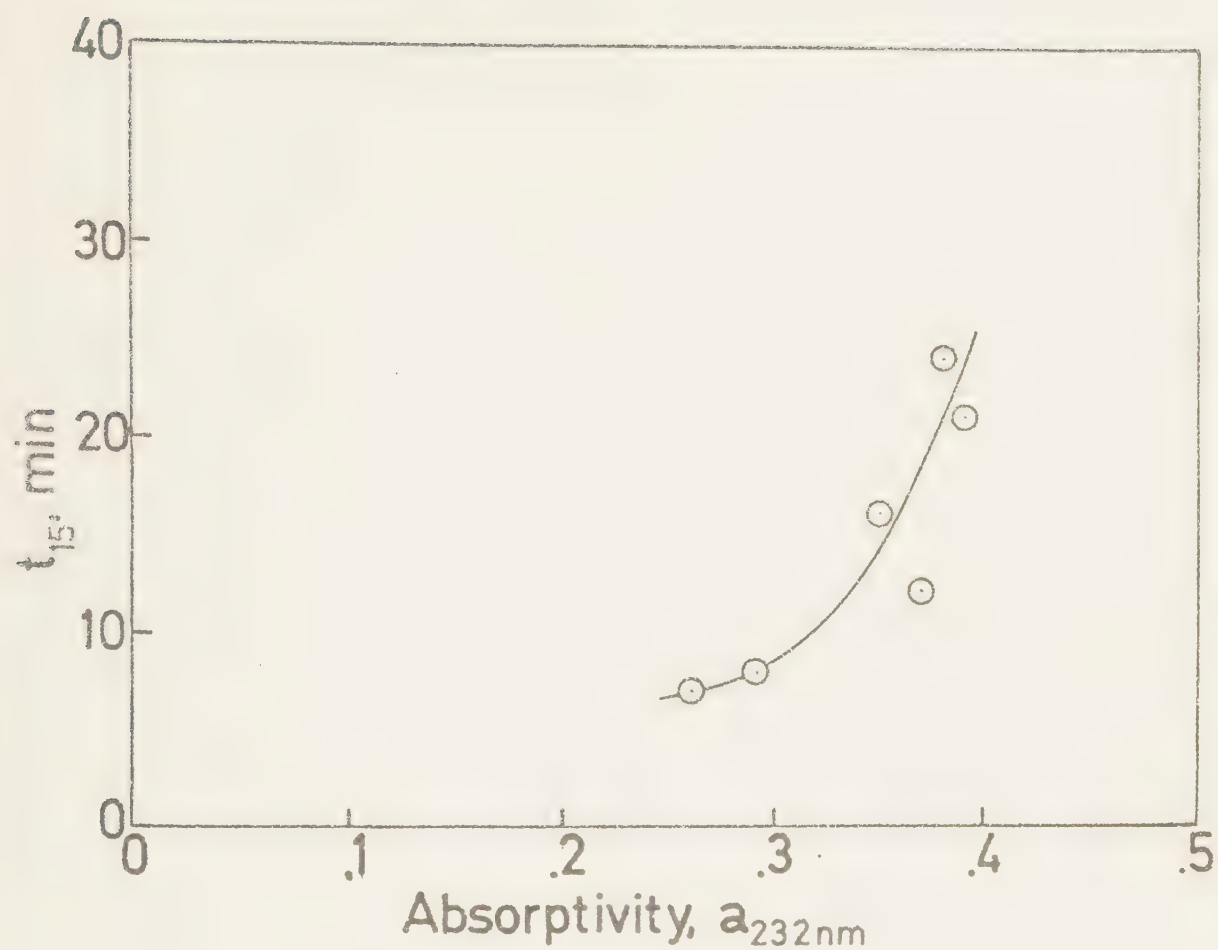


FIG. 4. Time for an iodine value drop of 15 units versus absorptivity $a_{232 \text{ nm}}$ for 6 soybean oils (Cu-1106P, 0.2 wt-% Cu in the oil, 6 atm, 185 C and 50 liter H_2/hr).

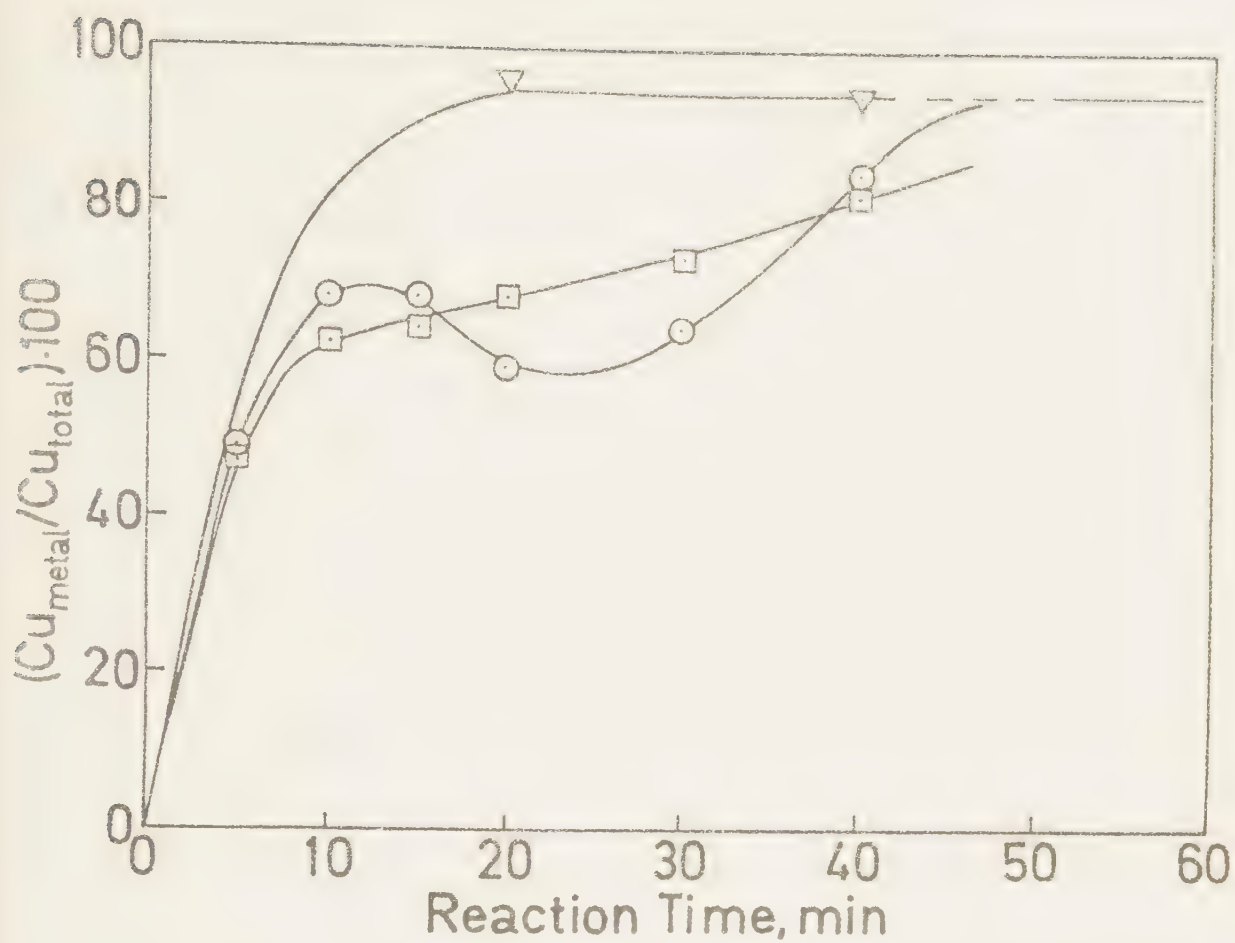


FIG. 5. Copper metal in Cu-1106P catalyst during hydrogenation of soybean oil at 3 atm and 185 C (X-ray diffraction analysis); $\square$ Dead-end, $\circ$ 50 liter H_2/hr , and $\triangle$ addition of water to the inlet flow, 50 liter H_2/hr .

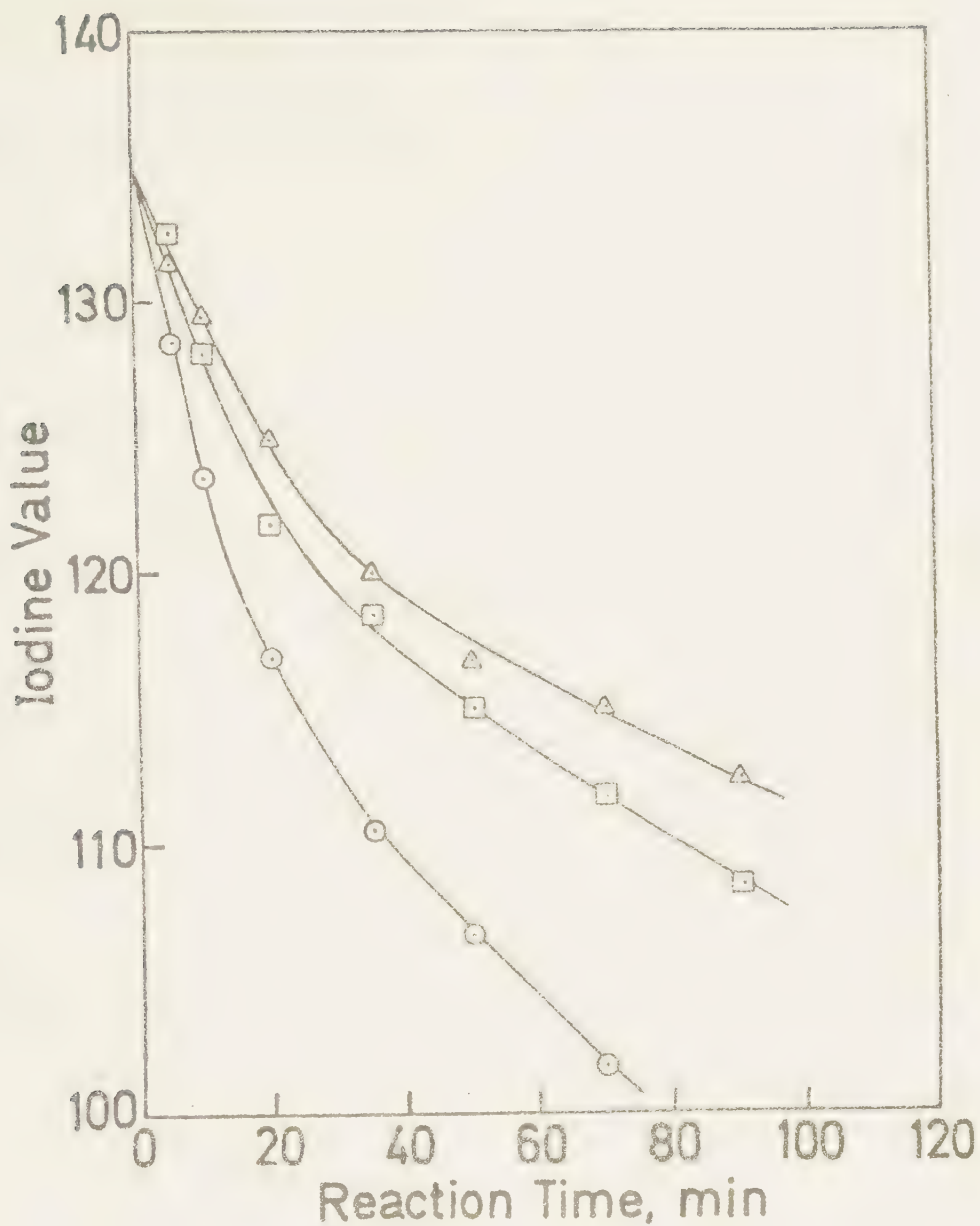


FIG. 6. Hydrogenation of soybean oil with Cu-1106P catalyst (0.1 wt-% Cu in the oil at 3 atm and 185 C);
 □ Dead-end, ○ 50 liter H₂/hr, and △ addition of water to the inlet hydrogen flow of 50 liter H₂/hr.

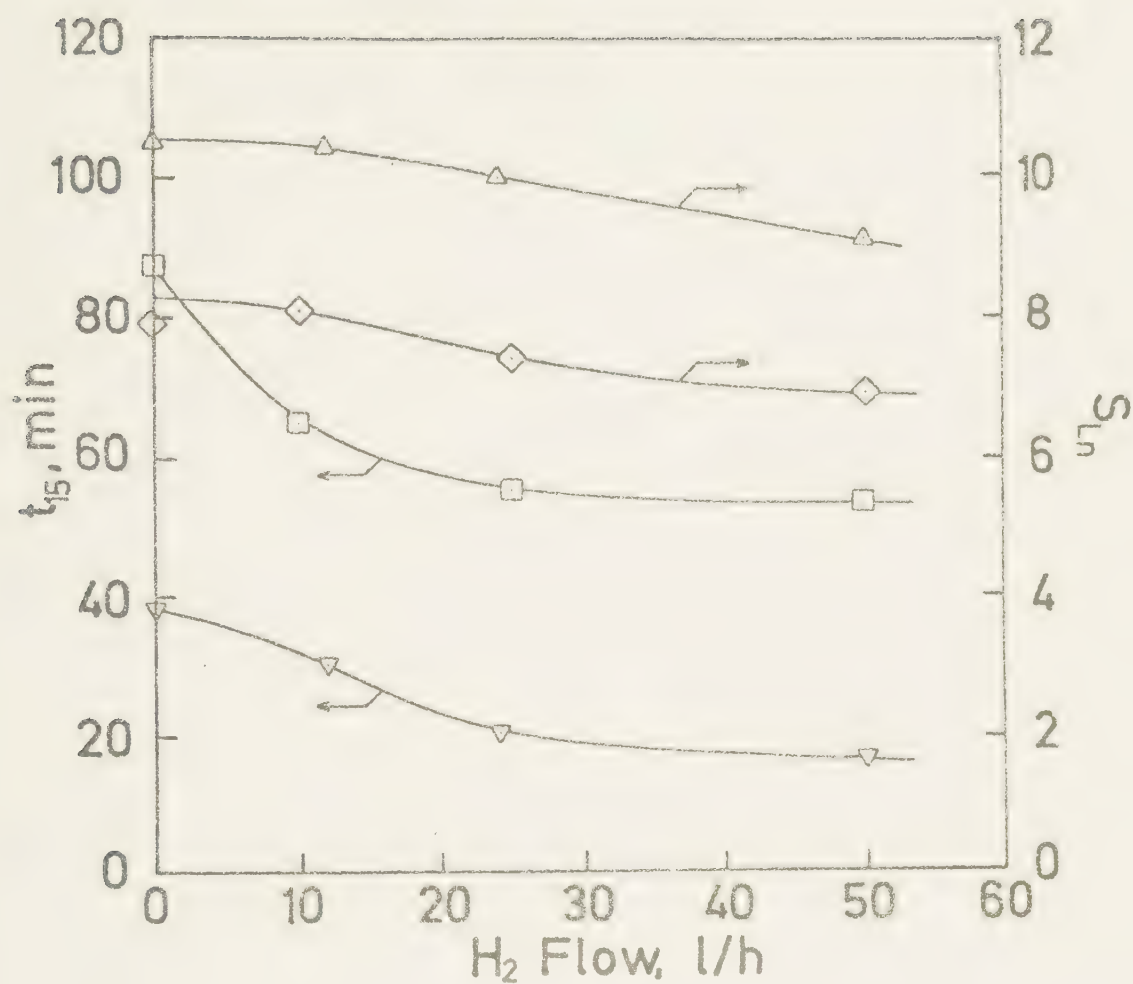


FIG. 7. Hydrogenation time and selectivity S_{Ln} versus the hydrogen flow. (Cu-1106P, 0.2 wt-% Cu, 6 atm, and 185 C); Soybean oil ∇ and $\triangle$ resp; Rapeseed oil $\square$ and $\diamond$ resp.

COPPER CATALYSTS IN THE SELECTIVE HYDROGENATION OF SOYBEAN
AND RAPESEED OILS: III. THE EFFECT OF PRESSURE WHEN USING
COPPER CHROMITE CATALYST

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Copper Catalysts in Selective Hydrogenation of Vegetable Oils

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ABSTRACT

The influence of pressure on the hydrogenation is investigated between 2-20 atm. The dependence between rate of reaction and pressure is complex with a maximum of rate at 6 atm in the pressure range below 14 atm. This is due to the fact that the catalyst reduction is simultaneous with the fat hydrogenation. The accumulation of conjugated dienes is measured and a mechanism proposal is presented.

INTRODUCTION

Hydrogenation catalysts based on copper possess high selectivity for hydrogenating the linolenate component of vegetable oils such as soybean, linseed and rapeseed oils. The linolenate is reduced 7 to 12 times faster than linoleate. Monoenes are not reduced, therefore the percentage of saturates is nearly unchanged during the process of hydrogenation (1,2).

Industrial autoclaves are usually designed for a maximum pressure of 11 atm and practically applied pressures range from 2 to 7 atm (3). The effect of the hydrogen pressure on the product composition in the hydrogenation of soybean and linseed oils as well as different actual methyl esters has been studied first of all at these pressure levels. Increasing pressure increases the rate of hydrogenation and decreases the percentage of conjugated dienes in the oil under hydrogenation (4,5). The linolenic acid appears to be reduced primarily through a conjugated intermediate, and this intermediate is desorbed less readily from the catalyst at a pressure of 5 atm than at 2 atm (5).

The low activity of copper catalysts, which is well known, can be compensated for by an increase of the hydrogen pressure above the interval generally used in the fat industry today. This is shown by the experiments of Mounts et al. (6), which are performed according to the dead-end procedure. Considerable advantages are obtained with respect to the reaction rate by

leading a flow of hydrogen gas through the autoclave during the hydrogenation process. Water and oxidation products are continuously removed from the oil and the autoclave, resulting in a decrease of catalyst poisoning (7).

The copper chromite catalysts are reduced during use (8). Catalytic activity coincides partly with the reduction of the catalyst, which proceeds in two periods if the water formed is removed from the oil and catalyst mixture. The reduced catalyst, consisting mostly of $\text{Cu/Cr}_2\text{O}_3$, shows activity first in the stage when the reduction water has been removed from the oil.

During that part of the process when the catalyst is being reduced, two hydrogen-consuming reactions are occurring at the surface of the catalyst. However, the amount of hydrogen required for the reduction of the catalyst is small in comparison to the amount of hydrogen converted in the hydrogen addition reaction. In a hydrogenation of 300 g oil with 0.1 wt-% Cu, charged in its divalent state, the consumption of hydrogen due to the reduction of the catalyst is ca. 0.11 liter H_2 (STP). An iodine value drop of 15 units corresponds to ca. 8 liter H_2 . Thus less than 2% of the hydrogen consumed is used for the reduction of the catalyst. Such a small proportion may not limit the supply of hydrogen for the hydrogen addition reaction. Concerning the activity of the catalyst, however, the activity contributions connected to the reduction of the catalyst are dominate during the first hydrogenation run of a catalyst lot. The rate of catalyst reduction thus affects the life-time of the catalyst and the order of priority between the two hydrogen-consuming reactions is of great importance.

The first step of the hydrogenation process, the reaction of conjugation, does not occur in the absence of hydrogen (9), but it requires no net supply of hydrogen. It is therefore favoured on a surface with a low hydrogen coverage. According to the mechanism, often referred to as the Horiuti-Polyanyi mechanism, an adsorbed molecule on such a surface has the choice between taking up a hydrogen atom from the surface or conversely giving a hydrogen atom to the surface (10). If a system of two methylen-interrupted double bonds is adsorbed on a surface with a low hydrogen coverage and no hydrogen atoms are available for a complete hydrogenation reaction, a conjugation of the two double bonds is thermodynamically favourable. A high rate of reaction requires a good supply of dissociatively adsorbed hydrogen at the catalyst surface. However, such a good supply also implies the risk of a fast catalyst reduction, which means a lower mean value of catalytic activity. In this report, the conditions of the catalyst surface with respect to the hydrogen coverage is discussed, firstly on the basis of a relation between hydrogen pressure and rate of reaction $-d(IV)/dt$.

EXPERIMENTAL PROCEDURES

Material

Hydrogenations were carried out with commercially refined and bleached soybean and rapeseed oils. The percentage of erucic acid in the different rapeseed oils was ca. 17%.

The catalysts used were two commercially supplied copper chromite catalysts from Harshaw Chemical Company, Cu-1106P (40% CuO, 47%

Cr₂O₃, and 10% BaO) and Cu-1800P (51% CuO and 47% Cr₂O₃) and a Raney-Cu catalyst from the firm Dr. Theodor Schuchardt.

Analytical Methods

The analytical methods used were previously described (8). Methyl esters were analyzed with a 9 ft. x 1/8 in. column packed with 7% BDS on 80/100 Chrom W. Iodine values were determined according to the Wijs method. The percentage of conjugated dienes in the oil was calculated from the UV absorption at 232 nm.

The amount of the crystalline copper metal in the samples of used Cu-1106P catalyst was estimated from X-ray diffraction measurements with the barium chromate phase as an internal standard.

Equipment and Operating Procedures

Hydrogenations were carried out in a 1 liter Parr apparatus. The oil to be hydrogenated and the appropriate amount of catalyst were charged into the autoclave. After flushing with nitrogen, the oil and catalyst mixture was heated to reaction temperature while stirring under reduced pressure. The reaction was started by admitting hydrogen into the bomb.

In all the experiments presented here, 300 g oil was hydrogenated at a stirrer rate of 1700 rpm and with a hydrogen flow through the oil of 50 liter/hr, measured after the outlet valve at 1 atm and 20 C. No hydrogen gas was recirculated. The volumetric mass transfer coefficient of the gas/liquid interface k_a at the mass

transfer conditions in this study has been found to be $k_a = 0.65 \text{ sec}^{-1}$. The experimental results are considered to be independent of the external mass transfer resistances.

RESULTS AND DISCUSSION

The Order of Priority between the Catalyst Reduction and the Hydrogen Addition

The Cu-1106P catalyst, 0.1 wt-% Cu in the oil, was reduced at 3 atm and 185 C in a prehydrogenated soybean oil, hydrogenated as far as possible with the same catalyst. The composition of the reduction medium was as follows: C16:0 10.2%, C18:0 3.4%, C18:1 72.1%, and C18:2 12.9%. The iodine value of the oil decreased less than 3 units, thus the reduction occurred with only a very small simultaneous hydrogen addition reaction. In all other respects the conditions were the same as those of the hydrogenation earlier performed for the study of the catalyst reduction during hydrogenation (8). According to the X-ray diffraction measurements, the formation of copper metal proceeds at a higher rate if no fat hydrogenation reaction occurs (Fig. 1). Thus a hydrogen consuming reaction occurring at the surface decreases the potential of catalyst reduction. The final reduction level is the same irrespective of whether hydrogenation occurs at the surface or not. The bleached soybean oil used in these experiments was very easily hydrogenated, therefore the effect of catalyst poisoning on the result is regarded as negligible.

The Effect of a Low Hydrogen Coverage

As the mass transfer resistances are negligible, the hydrogen coverage of the catalyst surface depends on the hydrogen concentration in the liquid phase, the ability of the catalyst to adsorb hydrogen from the liquid phase, and the rate of the hydrogen addition reaction.

The influence of a low hydrogen concentration in the liquid phase was shown experimentally as follows:

After 5 minutes of a normal hydrogenation run (rapeseed oil, Cu-1106P, 0.2 wt-% Cu in the oil, 185 C, and 6 atm) the hydrogen supply to the autoclave was interrupted for 15 minutes. The outlet valve remained open until the pressure reached atmospheric level. This procedure was repeated during the next 5 + 15 minutes. Samples were drawn from the autoclave, when necessary with the help of nitrogen gas.

The amount of conjugated dienes in the oil increased during the periods when the inlet valve was closed and decreased during the normal operation of the autoclave (Fig. 2). Thus, the accumulation of conjugated dienes is not only strongly dependent on the hydrogen concentration of the oil, as was earlier known, but also extremely sensitive to variations of that concentration. The formation of conjugated dienes is favoured by a low supply of hydrogen at the catalyst surface.

The Formation of Conjugated Dienes

The conjugation reactions start immediately upon the introduction of hydrogen gas to the oil and catalyst mixture. In the hydro-

generation with unused copper chromite catalyst, conjugated dienes are formed and accumulated in the oil during the first 10-20 minutes. The accumulation is different over different systems subjected to reduction. The accumulation of conjugated dienes when a separate copper(II)chromite phase is used (8) is small compared to the complete chromite catalyst with CuO present. Copper metal (Raney-Cu) forms practically no conjugated dienes at 6 atm (Fig. 3).

The percentage of conjugated dienes in the oil has a maximum, which decreases with the increase of the hydrogen pressure (Fig. 4). The time of the maximum also decreases with increasing pressure. The accumulation is low and independent of pressure at pressures above 13 atm.

The Effect of Pressure on the Rate of Reaction

Soybean oil was hydrogenated with unused Cu-1106P catalyst at different hydrogen pressures (0.05 wt-% Cu in the oil). Figure 5 shows the value $15/t_{15} \text{ min}^{-1}$ as a function of the hydrogen pressure p_{H_2} atm, where t_{15} is the time required for an iodine value drop of 15 units. In flow hydrogenations the hydrogen pressure p_{H_2} is regarded equal to the total pressure P . As mentioned in the introductory comments, the curve expresses the influence of two joint effects: the influence of pressure on the reaction rate at constant catalyst activity and the effect of pressure on the average catalytic activity during the first t_{15} minutes of the hydrogenation at p_{H_2} atm.

The mean rate of reaction increases with pressure up to about 6 atm, which is in accordance with the data in literature. The same normal relation between rate of reaction and pressure is valid above 14 atm. The difference of reaction rate between the different hydrogenation runs remains throughout the whole process, which is shown by the curve $22/t_{22}$ versus the hydrogen pressure.

The hydrogenation system used includes a hydrogen flow through the oil, which facilitates the removal of reduction water from the oil and the autoclave. The rate of water removal is considerably lower at pressures above the pressure level of saturated water vapour (ca. 11 atm/185 C and ca. 15 atm/200 C). The poisoning effect of water cannot be avoided to the same extent at hydrogenation above that level as is the case at lower pressures. The marked change of the graphs at 11-12 atm/185 C and 15-16/200 C respectively is the result of the water effect.

Catalytic activity is ascribed to the surface of an oxidic copper compound subjected to reduction and to the resulting copper metal, promoted by the underlying layer of oxidic support. The rate of catalyst reduction increases with the pressure p_{H_2} . Consequently the period of activity connected to the catalyst reduction is shorter at high pressure levels. To a certain extent, the effect of a fast catalyst reduction is compensated for by the fact that the rate of hydrogenation with a catalyst with a constant activity increases with pressure. Furthermore, the reduction of the oxidic compound means the formation of copper metal.

Above the pressure level of 12-13 atm the hydrogenation reaction is catalyzed by the reduced form of the catalyst. The mean rate of reaction in the interval 13-20 atm is proportional to $(p_{H_2} - 12)^{0.5}$. The pressure dependence exists mainly during the period of linolenate reduction. A catalyst lot used in a 40 minutes hydrogenation of soybean oil at 20 atm and 185 C was reused at 10 atm. The low value of $15/t_{15}$ obtained, 0.08 min^{-1} , includes the effect of double catalyst poisoning, but the difference between the oxidic and the reduced catalyst forms is fully clear. The metallic component contributes to the activity at pressures above 10-11 atm, but its contribution is decisive first at about 13 atm.

The rate maximum at 6 atm is ascribable to the activity of Cu/Cu^{I} combination (8). The contribution of the oxidic phase decreases with pressure. Judging from the accumulation of conjugated dienes, the oxidic surface makes a contribution up to a pressure of about 13 atm.

The Influence of Hydrogen Pressure on Selectivity

The simplified reaction model normally used for the calculation of the selectivity towards the linolenate component presupposes consecutive first order reactions, Trienes $\rightarrow$ Dienes $\rightarrow$ Monoenes. Here the selectivity S_{Ln} towards the linolenate of soybean oil in hydrogenation at different pressures has been calculated from the GLC composition according to the program given by Butterfield et al. (11). The values given here correspond to an iodine value drop of 15 units and the hydrogenation runs are the same as those represented in Figure 5 (Fig. 6).

The variations between the different levels of hydrogen pressure are small. However, from a mechanistic point of view, the conclusions of Vigneron et al. (5) concerning hydrogenation below 5 atm are confirmed. Due to the relatively low hydrogen coverage of the catalyst surface, the triene molecules are desorbed to a greater extent after the first step of hydrogen addition.

The Course of Reactions at the Catalyst Surface

Catalytic activity requires the ability to adsorb fatty molecules and the ability to activate hydrogen molecules present in the oil. The accumulation of conjugated dienes in the oil indicates that fatty molecules are adsorbed at the surface of the catalyst but, due to a hydrogen shortage, the hydrogenation reaction cannot be completed.

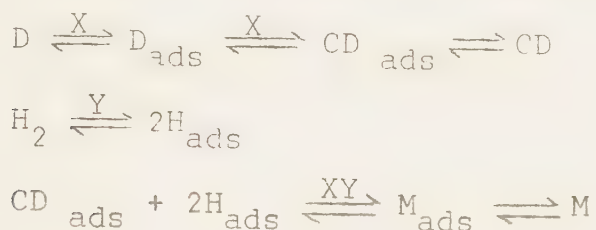
To judge from the accumulation of conjugated dienes, the conditions of adsorbing unsaturated fatty molecules are most advantageous at an oxidized phase of copper. As the presence of hydrogen is necessary, it is difficult to decide whether activation by partial reduction of the original catalyst surface is necessary or not, even if it is most probable. The dissociative adsorption of hydrogen is thus the rate-determining step of the process during the period of high reaction rate. Consequently, the ability of the catalyst to adsorb is decisive for the rate of hydrogenation. Since the two hydrogen-consuming reactions compete for the hydrogen adsorbed at the surface of the catalyst, the active sites involved in the two reactions are assumed to be the same. Therefore, being extensively

described in the literature, the reduction of copper(II)oxide may serve as a model for the reduction of the copper chromite catalyst.

The copper(II)oxide is reduced in three stages - induction, autocatalytic or acceleratory, and decay - and the reactions start on certain active nuclei (12). The reactions occur at the interface between the copper metal nuclei and the surrounding copper oxide phase. The hydrogen is presumed to chemisorb on the copper metal near the interface and to migrate to the interface (13) or to be adsorbed on copper atoms in contact with the oxide (12). The contact between the copper atoms and the oxide must be very close as acceleration of the reduction cannot be produced by stirring metal into the oxide or by placing metal as a layer on the oxide (12). The copper metal must be produced within the oxide phase by reduction or, for instance, by decomposition of copper(II)-formate.

The model is in all probability applicable to the part of the chromite catalyst consisting of copper(II)oxide crystallites and, concerning the close contact between copper atoms and adjacent oxide, even applicable to the rest of the catalyst. According to the model, the dissociative adsorption of hydrogen increases during the two periods of catalyst reduction. When the reduction is finished, the ability of the catalyst to dissociatively adsorb the hydrogen diminishes.

Thus, favourable conditions of adsorbing fatty molecules exist at an oxidized surface, perhaps activated by a limited reduction to copper metal (Surface X). Favourable conditions for dissociative adsorption of hydrogen exist at an oxide surface during reduction, i.e. when copper metal atoms are in close contact with adjacent oxide (Surface Y). The reaction of hydrogenation is shown in the following scheme:



where D is a system of two methylene-interrupted double bonds, CD is a system of two conjugated double bonds, and M is a monoene.

Above 12 atm the contribution of the copper phases subjected to reduction is low and the hydrogenation occurs mainly over a surface of copper metal on chromic oxide. If the copper content of the chromite catalyst is not totally reduced to metal, a positive contribution to the catalytic activity is implied. Our previous work has shown that about 5% of the copper content is chemically bonded to the chromic oxide even after a hydrogenation at 20 atm and 185 C for 120 minutes.

During the first minutes of a hydrogenation run the percentage of conjugated dienes in the oil is high and the hydrogen coverage of the catalyst surface is low. If the shortage of hydrogen is too marked, the risk of side reactions cannot be excluded. In the hydrogenation of methyl esters with copper chromite catalyst and deuterium, Koritala and Selke (9) found that the initial hydrogenation products contained only normal

hydrogen, i.e. hydrogen atoms were transferred from other molecules to the molecules under reduction. They proposed that hydrogen atoms of the dienes are first exchanged for deuterium atoms and then the hydrogen atoms are added to other diene molecules, which are hydrogenated. However, as far as we can see, the result would also imply that a step of self-hydrogenation is involved in the initial course of the hydrogenation process. Due to a low degree of hydrogen dissociation, hydrogen atoms temporarily bonded to the catalyst surface as a result of the adsorption of fatty molecules are added to other fatty molecules, which are hydrogenated. Such a hydrogen transfer was observed by Floyd et al. (14) when heating linolenic acid and its methyl esters in the presence of palladium. The donor molecules are hydrogenated in a consecutive step.

Conclusions

The dissociative adsorption of hydrogen is the rate-determining step during the periods of high catalytic activity. However, owing to the connection between the catalyst reduction and the activity, the effect of a relative hydrogen shortage on the rate of hydrogenation may be only partially eliminated by an increase of pressure within the pressure range of a normal industrial fat hydrogenation converter.

The question concerning the most active oxidation state of copper has no simple answer. According to the ESCA analyses of used copper chromite catalyst (8) all Cu^{II} ions are reduced within a few minutes of the process. Thus the most active surface contains only Cu^{I} and Cu^0 ions. The primary adsorption of the

fatty molecules occurs at the oxide part of the surface while hydrogen is adsorbed by the part with predominantly metallic properties. The function of hydrogen adsorption is common for any hydrogenation system using copper catalyst. The adsorption of the molecules subjected to reduction may however vary depending on the structure of the molecules.

The most ideal copper catalyst for the purpose of fat hydrogenation, based on our experiences with the copper chromite catalyst, seems to consist of small copper metal crystallites partially covering a layer of oxidic copper which is resistant to further reduction and from which the metallic copper has been formed.

Concerning the copper chromite catalyst below the pressure of 14 atm, the maximum rate of hydrogenation is obtained with fresh catalyst at 6 atm in the laboratory autoclave. If the difference of the hydrogen transfer gas/liquid is regarded, the corresponding pressure level of an industrial converter with a volumetric mass transfer coefficient $k_a = 0.05 \text{ sec}^{-1}$ is calculated to about 8 atm.

ACKNOWLEDGEMENTS

Thanks are due to Mrs. Birgitta Svensson for valuable experimental assistance and to Professor Sten T. Lundin for his continuous interest in this work. Financial support given in part by the Swedish Board for Technical Development is gratefully acknowledged.

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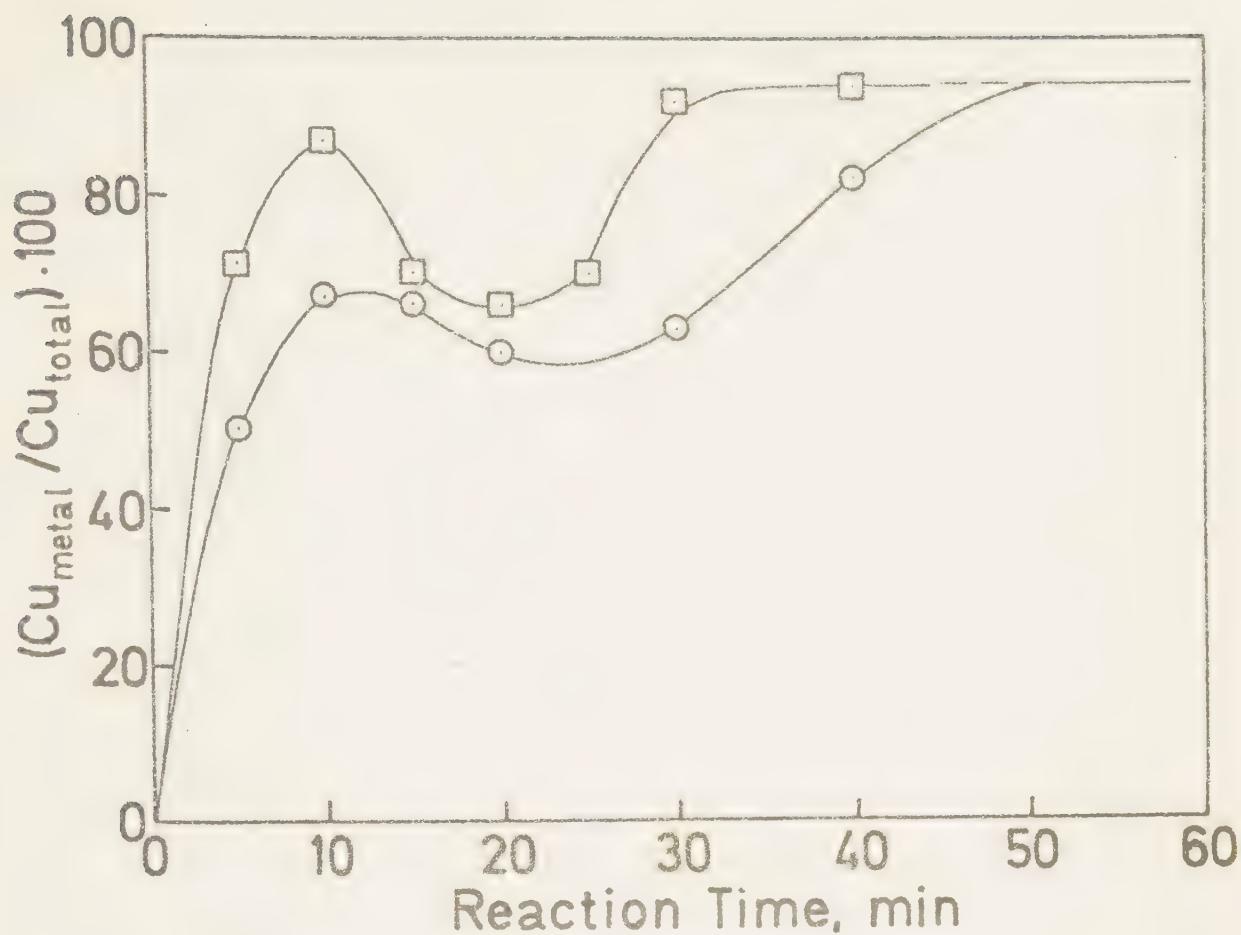


FIG. 1. Copper metal in Cu-1106P catalyst during reduction without hydrogenation ($\square$) and during reduction with a simultaneous hydrogenation reaction ($\circ$); 0.1 wt-% Cu, 3 atm, and 185 C.



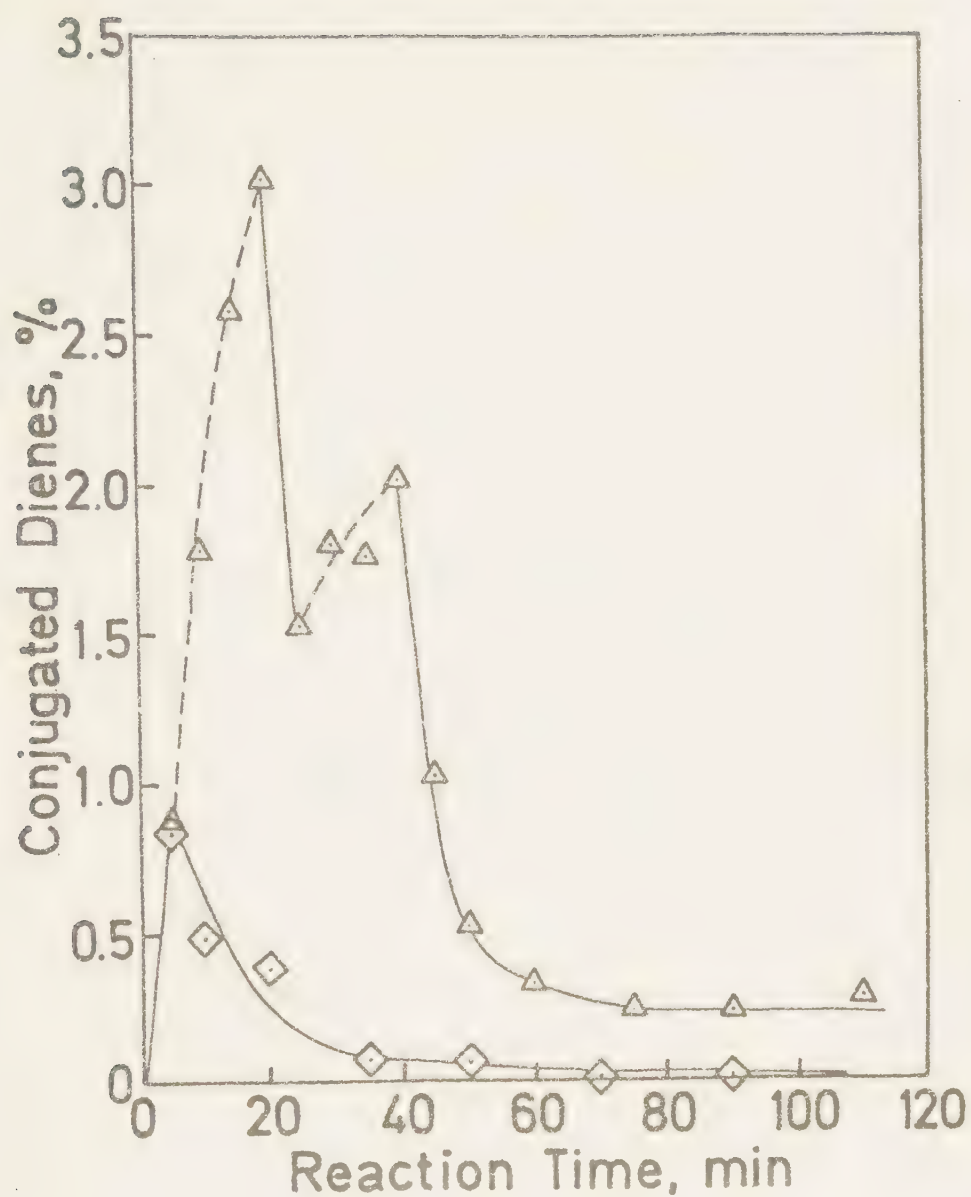


FIG. 2. Accumulation of conjugated dienes during normal operation (—) and during hydrogen shortage (-----) in rapeseed oil (Cu-1106P, 0.2 wt-% Cu, 185 C, and max. 6 atm H_2 -pressure).

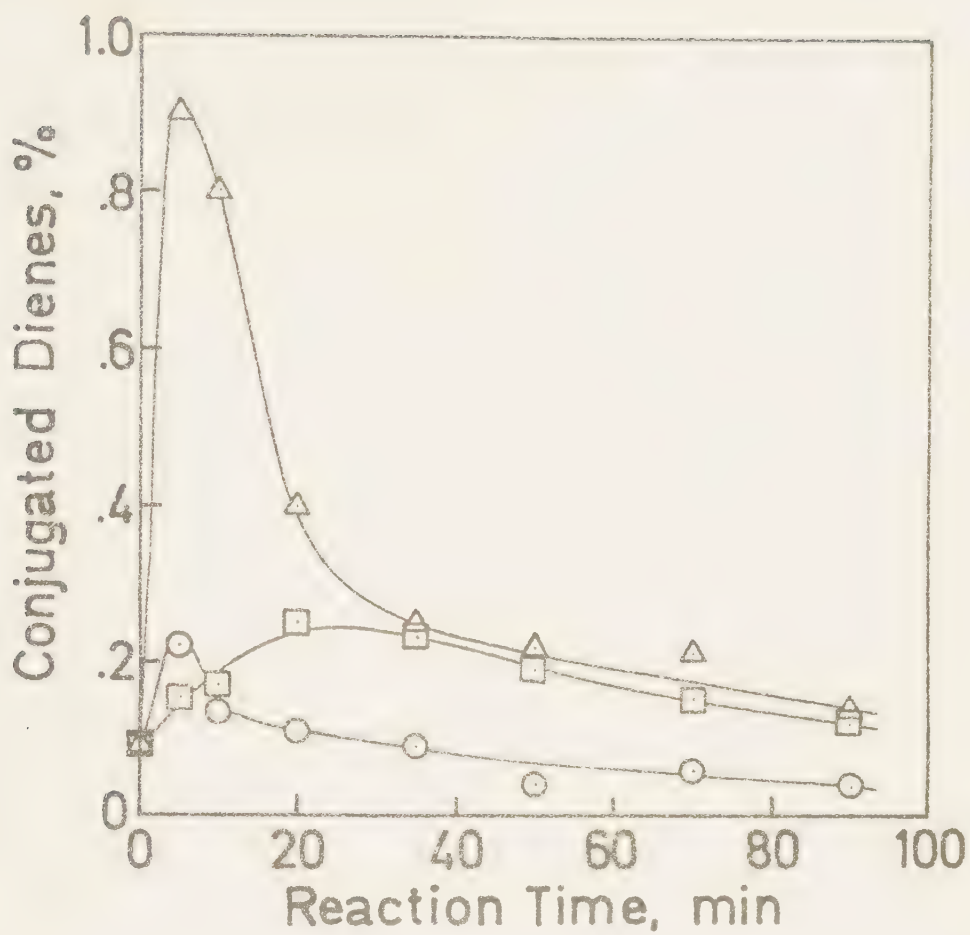


FIG. 3. Conjugated dienes in rapeseed oil during hydrogenation at 185 C and 6 atm with original Cu-1800P, 0.3 wt-% Cu (Δ), CuCr_2O_4 , 0.3 wt-% Cu ($\square$), and Raney-Cu 1.2 wt-% Cu in the oil (O).

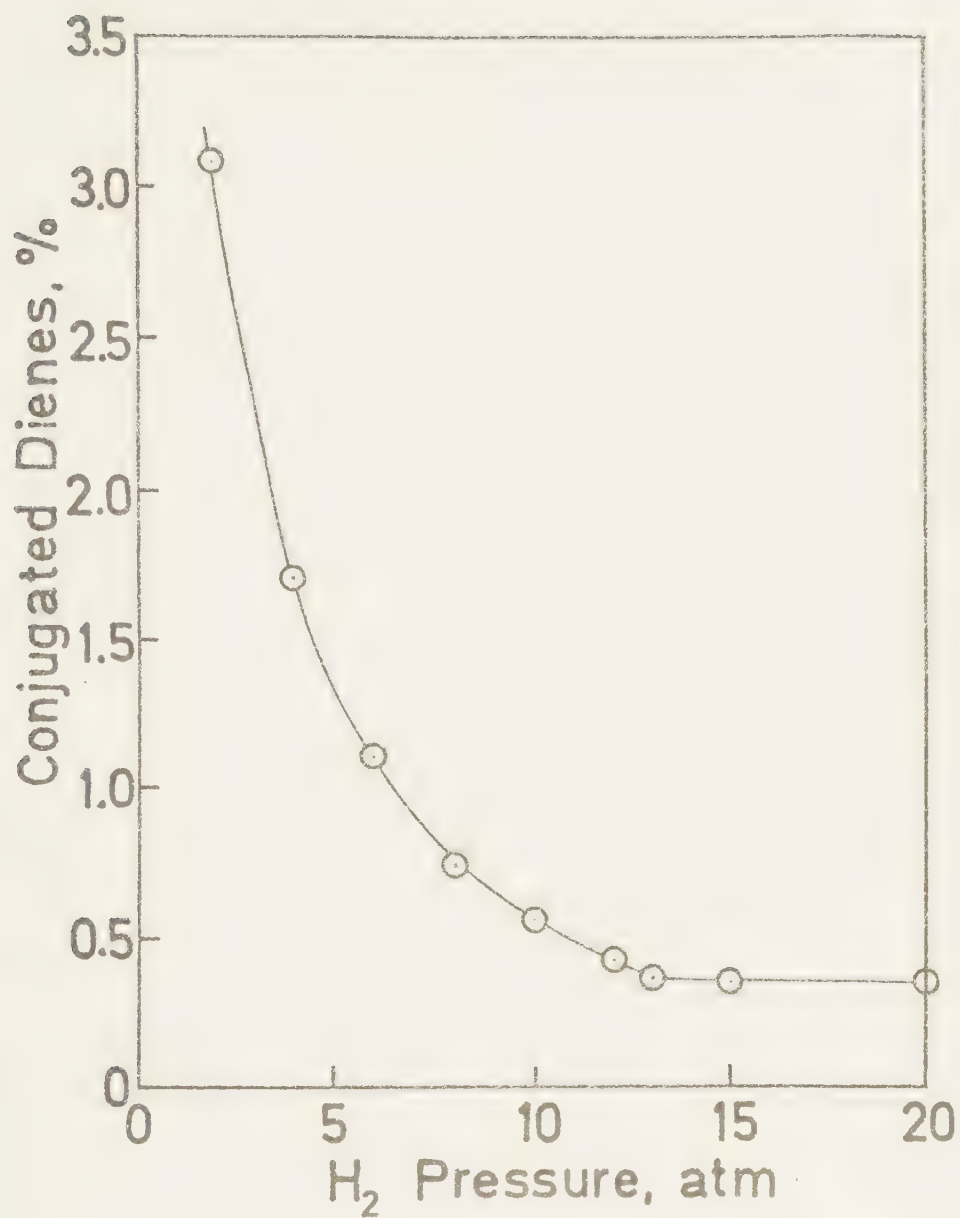


FIG. 4. Maximum percentage of conjugated dienes (UV absorption) versus the hydrogen pressure (Cu-1106P, 0.5 wt-% Cu in the oil and 185 C).

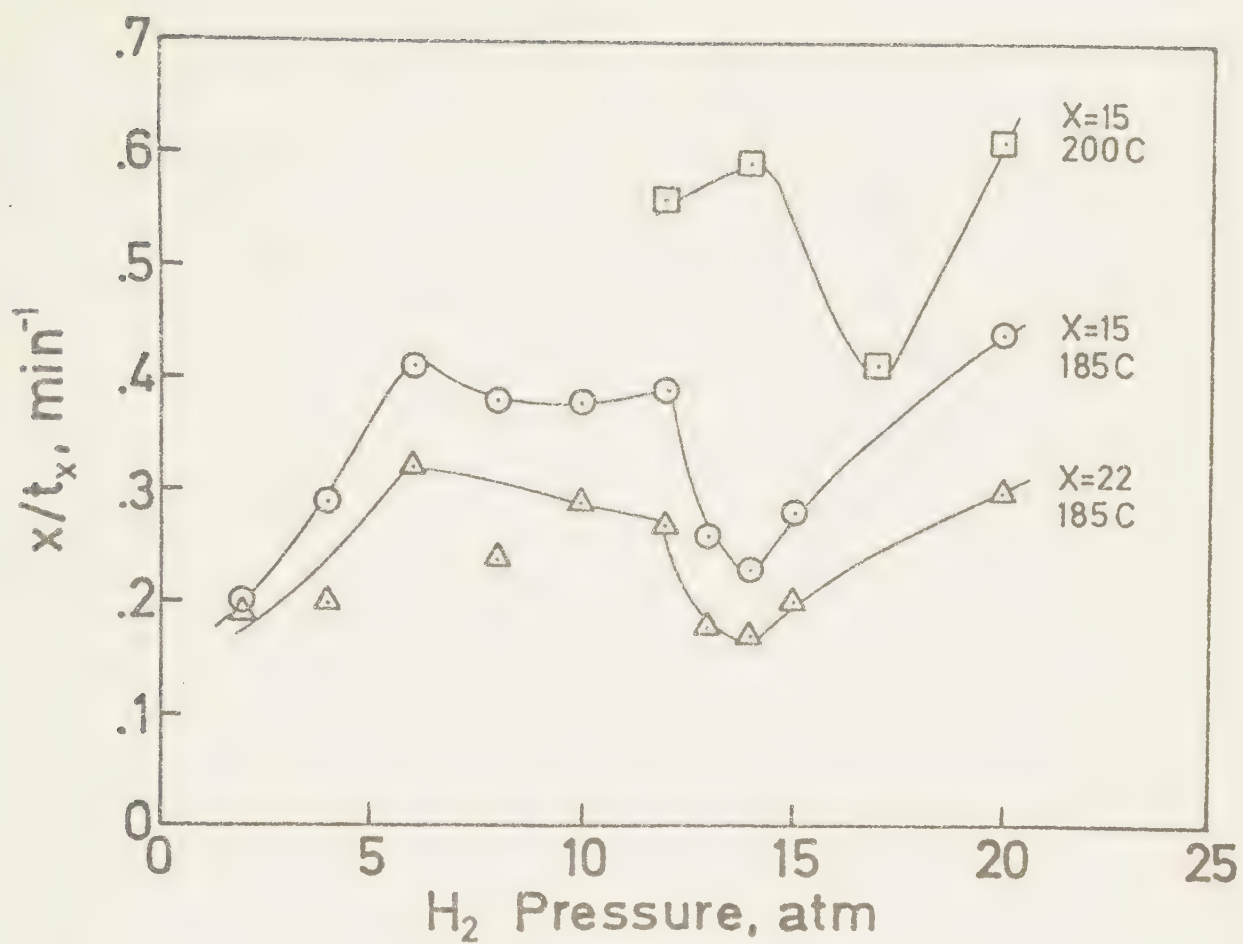


FIG. 5. Effect of hydrogen pressure on the mean rate of reaction in the hydrogenation of soybean oil (Cu-1106P, 0.05 wt-% Cu in the oil, and 185°C).

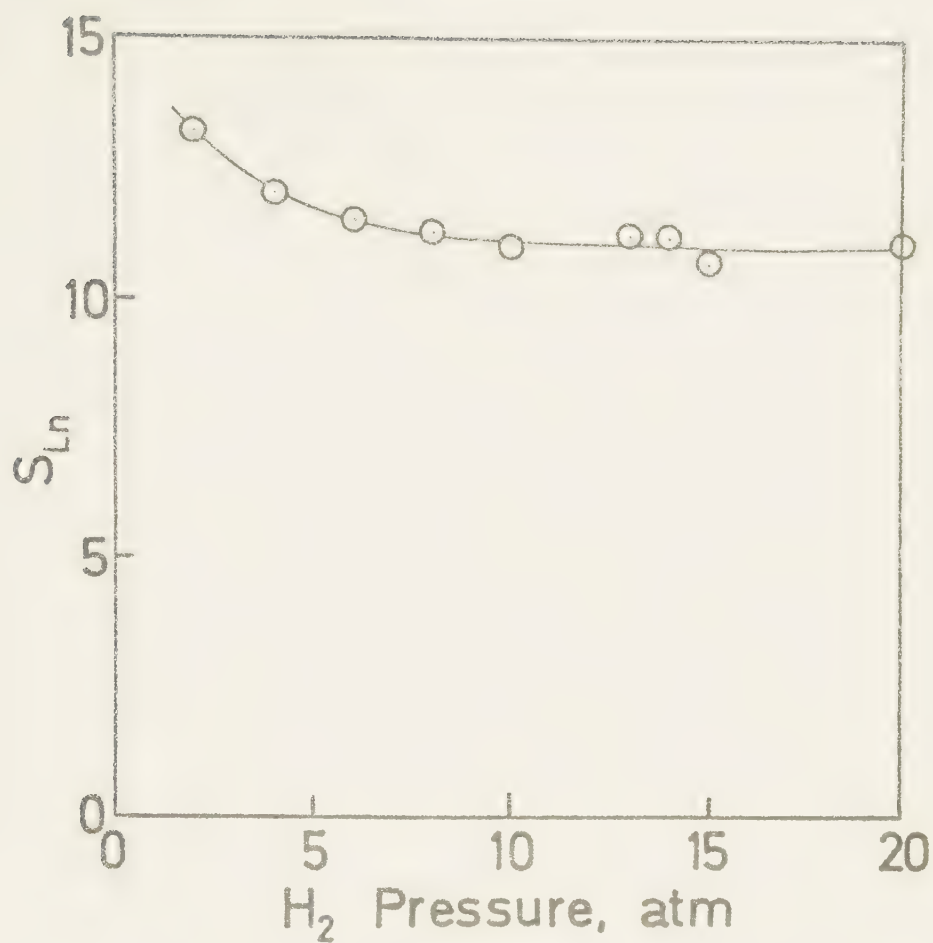


FIG. 6. Effect of hydrogen pressure on the selectivity S_{Ln} in the hydrogenation of soybean oil (Cu-1106P, 0.05 wt-% Cu in the oil, and 185 C).

COPPER CATALYSTS IN THE SELECTIVE HYDROGENATION OF SOYBEAN
AND RAPESEED OILS: IV. COPPER ON SILICA GEL, PHASE COMPOSITION
AND PREPARATION

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Copper Catalysts in Selective Hydrogenation of Vegetable Oils

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ABSTRACT

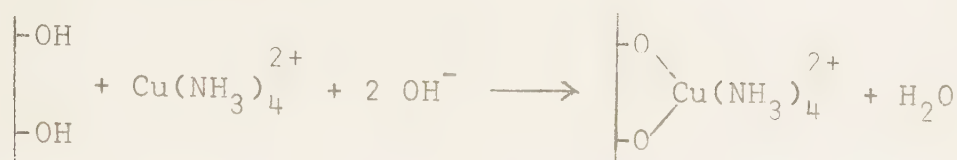
The phase composition of the copper on silica gel catalyst was studied with X-ray diffraction analysis. Activity measurements showed three periods of activity, the first two of which were ascribed to a copper surface subjected to reduction and the third one to the reduced form of the catalyst. The hydrogenation reaction over the Cu/SiO_2 catalyst has a complex pressure dependence with a rate maximum at 6 atm in the low pressure range. The preparation of the catalyst was studied. On the basis of a proposed reaction model, a mixture catalyst was prepared and tested with good results. In rapeseed oil hydrogenation the Cu/SiO_2 catalysts were shown to be superior to the copper chromite catalysts. In soybean oil the two types of catalyst were rather equivalent.

INTRODUCTION

Hydrogenation catalysts based on copper possess high selectivity for hydrogenating the linolenate component of vegetable oils like soybean, linseed and rapeseed oils. Linolenate is reduced 7 to 12 times faster than linoleate. Monoenes are not reduced, therefore the percentage of saturates is scarcely changed during the process of hydrogenation (1,2). The copper is usually charged into the oil as divalent oxidic compounds, which are partly reduced to metal during use. Two active forms of copper have been detected in a study of the copper chromite catalyst performed at this laboratory (3). A mixture of copper metal and copper(I)chromite showed activity mainly during its reduction, while the resulting copper compound, noted as $\text{Cu/Cr}_2\text{O}_3$, first became active in a stage of the process where the reduction of the catalyst was completed and water no longer was being generated. Conditions favourable for adsorbing fatty ester molecules exist first of all at the oxidic copper surface, which is possibly activated by a limited reduction to metal (4). The dissociative adsorption of hydrogen is facilitated by copper metal atoms in close contact with adjacent oxide. Thus, judging from earlier work with the copper chromite catalyst, the most ideal copper catalyst, characterized by a constant activity for fat hydrogenation, consists of small copper metal crystallites partially covering a layer of oxidic copper, which is resistant to further reduction. The metallic copper has been formed by reduction of the oxidic phase.

The experiments presented here were carried out in order to construct such a catalyst surface on a support material.

Silica gel adsorbs copper ions from ammoniacal solutions in the form of tetrammine complex (5-9). One type of copper ammine polysilicate is formed.



During washing and activation in air at 300-600 C most of the ammonia is released and coordinatively unsaturated surface ions of Cu^{2+} are generated (9). The copper adsorbed in this way is more tightly bonded to the gel than in the case of impregnation from neutral solutions. Part of the copper content is resistant to complete reduction in hydrogen gas (10).

The method of copper adsorption onto silica gel from ammoniacal solution has been used by Koritala in the preparation of copper catalysts for the hydrogenation of soybean oil (11). A later modified procedure includes however also a pure precipitation step (12), in which the unadsorbed copper ions are precipitated onto the gel by the dilution of the adsorption solutions with water. We have tested the catalyst prepared in this way for rapeseed oil hydrogenation and have found that it has a high activity. The method of preparation has been modified for that purpose.

EXPERIMENTAL PROCEDURES

Materials

The hydrogenations were carried out with commercially refined and bleached rapeseed and soybean oils. The rapeseed oils used in most of the hydrogenation experiments were of medium quality with respect to the erucic acid content (ca. 17%). The oil used in the product evaluation was a "zero-erucic" rapeseed oil, containing only 0.5% erucic acid component.

The Cu/SiO_2 catalysts were made from copper(II)nitrate trihydrate (p.a.) and ammonium hydroxide (p.a.). The support material was supplied from Davison Chemical Division, W.R. Grace & Co (MS-Gel 951, specific surface area $600 \text{ m}^2/\text{g}$, pore volume $1 \text{ cm}^3/\text{g}$, and average pore diameter $67 \text{ \AA}$). In addition to the catalysts prepared here, a sample of Cu/SiO_2 catalyst from W.R. Grace & Co, described as "CuO catalyst for vegetable oils hydrogenation" (5.03 wt-% CuO, 94.8 wt-% SiO_2 , specific surface area $250 \text{ m}^2/\text{g}$, pore volume $0.79 \text{ cm}^3/\text{g}$, and average pore diameter $126 \text{ \AA}$) was used. The copper chromite catalyst used for comparison was supplied from Harshaw Chemical Company (Cu-1106P; 40% CuO, 47% Cr_2O_3 , and 10% BaO; $40 \text{ m}^2/\text{g}$).

Analytical Methods

The analytical methods have been previously described (3). Methyl esters were analyzed with a BDS column. Iodine values were determined according to the Wijs method. The percentage of conjugated dienes in the oil was calculated from the UV absorption at 232 nm.

The X-ray diffraction analyses of catalyst samples were performed with a Philips PW 1050/25 diffractometer (Cu-K radiation, 45 kV and 24 mA). The ESCA measurements were performed with an AEI ES10 electron spectrometer. The amount of copper adsorbed at the silica gel was determined by atomic absorption spectroscopy.

Catalyst Preparation

The Cu/SiO₂ catalysts were prepared according to the principal procedure given by Koritala (12), in which ammonium hydroxide is added to an aqueous solution of Cu(NO₃)₂ · 3 H₂O. The copper hydroxide precipitate is redissolved. The silica gel is added to the copper solution and part of the blue ions are adsorbed onto the gel. The remainder of the copper ions is precipitated onto the gel as copper hydroxide when the solution is diluted with distilled water. The procedure is repeated once. The pale blue catalyst is dried over night at 110 C and calcined at 350 C for 2 hours.

The composition of the adsorption solution has been varied within this study. The catalyst prepared according to the Koritala procedure (12) is prepared from 2 x 25 ml of an aqueous solution containing 2 x 1 g of Cu(NO₃)₂ · 3 H₂O and to which 2 x 1.44 ml of a 25% NH₄OH solution has been added. The solutions are diluted to 200 ml and 400 ml respectively.

Equipment and Operating Procedures

Hydrogenations were carried out in a 1 liter Parr apparatus. The oil to be hydrogenated and the appropriate amount of

catalyst were charged into the autoclave. After flushing with nitrogen, the oil and catalyst mixture was heated to reaction temperature while stirring under reduced pressure. The reaction was started by admitting hydrogen into the bomb.

In all the experiments presented here, 300 g oil was hydrogenated at a stirrer rate of 1700 rpm and with a hydrogen flow through the oil of 50 liter/hr, measured after the outlet valve at 1 atm and 20 C. No hydrogen gas was recirculated. The volumetric mass transfer coefficient k_a of the gas/liquid interface at the mass transfer conditions in this study has been found to be $k_a = 0.65 \text{ sec}^{-1}$ (13). The experimental results are considered to be independent of the external mass transfer resistances.

RESULTS

The Phase Composition of the Cu/SiO_2 catalyst

The phase composition of the Cu/SiO_2 catalyst was studied on the basis of a catalyst sample prepared from $\text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O}$ according to the procedure given by Koritala. Within this study, that type of supported catalyst contains the highest percentage of copper.

The X-ray diffraction spectrum shows, besides the peak of amorphous silica gel, a broad peak around $35^\circ 2\theta$ ($d = 2.56 \text{ \AA}$), which indicates the presence of small CuO crystallites. The electron microscopy pictures show small crystal needles

(Fig. 1). The BET surface area of the emerald green material is ca. $350 \text{ m}^2/\text{g}$.

The catalyst is reduced during use and water is generated. In the soybean oil the colour changes from green to grey-black even at 3 atm H_2 pressure. Crystalline phases of Cu metal and Cu_2O are formed during the first few minutes.

In rapeseed oil at 3 atm H_2 pressure, however, the colour variation is limited to a change from emerald to olive-green. Only Cu_2O appears in the X-ray spectra of samples used for 120 minutes. Catalyst samples used in rapeseed oil hydrogenation with H_2 pressure above 20-25 atm are black and contain a Cu and Cu_2O mixture. Independent of the oil hydrogenated, the black samples change to green when exposed to air at room temperature.

Catalyst samples from rapeseed oil hydrogenation at 3 atm have been subjected to ESCA measurements in order to find out if Cu metal is formed even at low H_2 pressures. No Cu^0 atoms were detected. Prior to the ESCA work, the catalyst must be subjected to a careful washing procedure in chloroform. From the change of colour it follows that Cu metal of reduced Cu/SiO_2 catalyst is readily re-oxidized. Thus, the result obtained does not exclude the existence of Cu^0 atoms during the hydrogenation.

Obviously the copper of the Cu/SiO_2 catalyst is more resistant to reduction than that of the copper chromite catalyst, in which 95% of the copper content is reduced to metal.

Changes of the Catalyst Activity during Hydrogenation

The activity of the Cu/SiO_2 catalyst as a function of the reaction time was determined as previously described for the copper chromite catalyst (3). A number of hydrogenation runs were interrupted at different reaction times. The catalyst lot of each run was separated from the oil and charged into soybean oil, which was hydrogenated at 6 atm and 185 C. The activity was estimated from the value of $1/t_3 \text{ min}^{-1}$, where t_3 was the time required for an iodine value drop of 3 units. The activity of the unused catalyst charged directly into original soybean oil was set to 100%.

The activity curve of a Cu/SiO_2 catalyst, prepared according to the procedure given by Koritala, used in soybean oil at 3 atm and 185 C (0.1 wt-% Cu in the oil) shows three periods of activity (Fig. 2). The curve is similar to that obtained with the use of copper chromite catalyst in soybean oil at 3 atm. Regarding that catalyst, the two first periods were ascribed to the two periods of copper metal formation. The third period was ascribed to the reduced catalyst, $\text{Cu/Cr}_2\text{O}_3$, the activity of which appears in a stage when the reduction of the catalyst is finished and the water generated has been removed from the oil. The interferences of the crystalline phases of the Cu/SiO_2 catalyst during the hydrogenation are too small to be used to estimate the copper metal content in the catalyst samples.

The activity curve of the catalyst used in rapeseed oil at 6 atm H_2 pressure shows only two periods of activity within

the time interval 0-60 minutes. Also in this respect, the Cu/SiO_2 catalyst behaves similarly to the copper chromite catalyst.

The Effect of Hydrogen Pressure on the Rate of Reaction

Figure 3 shows the mean rate of reaction $15/t_{15}, \text{ min}^{-1}$, as a function of the hydrogen pressure p_{H_2} , atm, where t_{15} is the time required for an iodine value drop of 15 units (Cu/SiO_2 with 17% Cu, 0.12 wt-% Cu in rapeseed oil).

The pressure level of saturated water vapour at the reaction temperature (ca. 11 atm/185 C and ca. 15 atm/200 C) is characterized by a rate maximum. The effect of water is thus as obvious as was earlier shown for the copper chromite catalyst (4). Above that pressure level, the rate of water removal is considerably lower and the water generated during the catalyst reduction stays longer within the oil bulk, causing catalyst poisoning.

Cu metal has been detected as a crystalline phase after hydrogenation at H_2 pressures above 20-25 atm (185 C). The mean rate of reaction over the grey-black catalyst surface increases with pressure in the interval studied $20 < p_{\text{H}_2} < 32$ according to the equation

$$15/t_{15} = k \cdot (p_{\text{H}_2} - 14.5)^{0.5} \quad [1]$$

This equation is like that of Cu-1106P in soybean oil (4), which is valid in the range $13 < p_{\text{H}_2} < 20$ (185 C)

$$15/t_{15} = k' \cdot (p_{\text{H}_2} - 12.0)^{0.5} \quad [2]$$

The contribution from the metallic phase of copper to the catalyst activity thus appears at a somewhat higher pressure with the use of the Cu/SiO_2 catalyst.

The hydrogenation performed below 20 atm H_2 pressure proceeds for the most part over an oxidic catalyst surface, i.e. a surface containing monovalent and probably also metallic copper. A maximum rate is obtained at 6 atm, a point where the product between catalyst activity and hydrogen concentration of the oil is optimal.

The Effect of Pressure on the Selectivity

The selectivity S_{Ln} towards the linolenate component of the rapeseed oil has been calculated from the GLC composition according to the program given by Butterfield et al. (14), using the simplified model of reaction including consecutive first order reactions. The values given in Figure 4 correspond to an iodine value drop of 15 units.

The S_{Ln} value is only slightly dependent on the H_2 pressure. The level of selectivity, however, is lower than that reported for soybean oil hydrogenation. The difference is to be ascribed to the different oil compositions and not to the catalyst used. Values from different oils cannot be compared. The product composition at different stages of the reaction at 6 atm is shown in Figure 5. The initial increase of the percentage of linoleic acid ester, including 1-2%, is fully comparable with that of a typical soybean oil hydrogenation.

Basic Principles for the Catalyst Preparation

The catalyst preparations described here are based on the following assumptions: the first copper ions that are adsorbed onto the silica gel from the ammoniacal solution are bonded directly to the support material and will constitute the oxidic part of the partly reduced catalyst surface. The strength of the bonds between the copper ions and the support depends on the excess of NH_4OH in the adsorption solution. A low excess results in relatively weak bonds, like those of impregnation. The copper precipitated onto the gel in connection with the dilution of the ammoniacal solution forms less stable CuO crystals at the surface. Thus, a catalyst surface produced in a solution with a low concentration of copper and a high excess of NH_4OH shows predominantly oxidic properties.

The effect of the calcination temperature on the activity of the resulting material was evaluated in a primary stage in soybean oil hydrogenations with Cu/SiO_2 - 17% Cu. The activity is independent of the temperature in the interval 325 - 500 C (Fig. 6).

The Conditions of Cu Adsorption

The composition of the adsorption solution - the $\text{Cu/NH}_4\text{OH}$ ratio and the amount of copper charged - was varied in a series of catalyst preparations. The activity values of the catalysts produced were evaluated in rapeseed oil hydrogenation. 8 g of catalyst material was charged per 300 g of oil. The catalyst activity per wt-% Cu in the oil as a function of the NH_4OH excess in the adsorption is shown in Figure 7. The

activity is estimated from $1/(t_{15} \cdot C_{\text{Cu}})$, min^{-1} , where t_{15} is the time required for an iodine value drop of 15 units, min, and C_{Cu} is the amount of Cu charged in the oil, wt-% Cu. The excess of NH_4OH has been calculated on the basis that every Cu^{2+} ion corresponds to four NH_3 molecules.

The catalyst activity per unit Cu increased with the excess of NH_4OH . If too strong an alkaline solution was used, it resulted however in an almost inactive catalyst. The maximum percentage of conjugated dienes during the hydrogenation runs increased with the excess of NH_4OH too, which is in accordance with the assumption that the surface is getting more and more oxidic properties.

The most active catalyst was prepared as follows: 5.75 ml of an ammonium hydroxide solution (25 wt-% NH_4OH) was added to 100 ml of water containing 2 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, at which point the precipitate of copper hydroxide is dissolved. 10 g of silica gel was added and the volume was diluted to 800 ml with water. The colourless liquid was poured off and a new batch of the copper solution was added to the gel. The volume was increased to 1600 ml before filtration, washing with water, drying at 110 C over night, and calcination in air at 350 C for 2 hours. The catalyst contained about 10 wt-% copper.

The activity, measured per gram Cu in this test, was about two times the activity of the catalyst prepared according to the procedure given by Koritala, which used a NH_4OH excess of ca. 1.8 mol/liter solution.

Mixtures with Two Catalysts

In the proposed reaction model, the catalyst surface represents two properties. The fatty molecules need not desorb between the conjugation and the hydrogen addition steps. However, one possibility for improving the activity per g of copper charged into the oil consists of combining two catalyst materials, one is constructed to produce conjugated dienes (the oxidic component of the surface) and the other one to hydrogenate the conjugated dienes produced (the copper metal component). In such a system, the fatty molecules have to desorb and re-adsorb before the reaction is completed. The advantage of such a catalyst system is that the two catalyst phases may be optimized independently.

Experiments were carried out with a mixture of two Cu/SiO_2 catalysts. Type A, in which the copper is more strongly bonded to the support, was represented by the catalyst supplied from Grace & Co (4% Cu). Type B, in which the average bond between Cu and the support is weaker, was represented by the Cu/SiO_2 catalyst containing 17% Cu. The time required for an iodine value drop of 15 units in rapeseed oil with a catalyst mixture, where the ratio between the amounts of copper charged as A and B was 2:1, was 47% shorter than if the same amount of copper was charged as catalyst A only and 34% shorter than if all the copper was charged as catalyst B (Fig. 8).

Metal-promoted Cu/SiO₂ Catalyst

The catalyst activity is highest during catalyst reduction. Accumulation of conjugated dienes indicates however a hydrogen shortage on the catalyst surface. The supply of dissociatively adsorbed hydrogen can be increased by addition of a metal that has an unfilled d-orbital.

The method of catalyst preparation involving NH₄OH allows the addition of metals other than copper, provided that the metal hydroxides are soluble in an NH₄OH excess. Studied here were the effects of the additions of chromium, cobalt and zinc from the first long period and silver from the second one. 2 wt-% metal based on the amount of copper was added to the adsorption solutions resulting in a catalyst with 17 wt-% Cu. From the results of Moulton et al. (15) concerning the addition of nickel to a CuCr-catalyst, the effect of a nickel addition was regarded as known. Due to the risk of contaminating the autoclave with this active but hardly selective metal, nickel was avoided in those experiments.

The promoted catalysts were tested in soybean oil hydrogenation. Only the addition of cobalt gave an enhanced catalyst activity (Fig. 9). The selectivity S_{Ln} was as high as that of the original Cu/SiO₂ catalyst in soybean oil ($S_{Ln} = 10.9$). From a technical point of view, the increase of activity by the addition of cobalt was regarded as too small to be interesting. The toxicity of cobalt is unfavourable as well.

Comparative Tests

The copper chromite catalyst, Harshaw Cu-1106P, used for comparison in this report was the best catalyst in a comparison test performed at this laboratory using soybean and rapeseed oil hydrogenation. Ten commercially supplied catalysts, selected from different catalyst firms, were tested. The comparison took into consideration the degree of copper exploitation, noted as the ratio $100/(t_{15} \cdot C_{Cu})$, min^{-1} . The reaction conditions were 6 atm H_2 pressure, 185 C, and a hydrogen flow of 50 liter/hr. The re-using properties were not considered.

The comparative tests presented here included four different catalysts:

- A) Cu-1106P - 29.9% Cu
- B) Cu/SiO₂ (Koritala) - 16.8% Cu
- C) Cu/SiO₂ - 10.1% Cu
- D) Cu/SiO₂ (mixture) - 6.7% Cu

The preparation of the catalyst C was described earlier in this report as well as the composition of the catalyst mixture D.

Table I shows the result of a comparison between the catalyst A and B. These catalysts are rather equivalent in the respect of soybean oil, but the Cu/SiO₂ catalyst offers considerable advantages in the hydrogenation of rapeseed oil.

The four catalysts A-D were compared in rapeseed oil hydrogenation (Table II). The oil used here was somewhat easier to hydrogenate than that of Table I (required a smaller amount of catalyst). The copper content is best used in the form of Cu/SiO_2 (10.1% Cu). However, the catalyst B and D were rather equivalent in the test, in spite of the fact that catalyst D was superior to B in the experiment in which the composition of the mixture was chosen. Thus, the order of precedence of the catalysts is not absolute, but may vary depending on the type and concentration of dominating catalyst poisons.

The difference between the copper chromite and the Cu/SiO_2 catalysts in rapeseed oil hydrogenation is partly ascribed to the resistibility of catalyst poisoning. The reaction time t_{15} in the hydrogenation of rapeseed oil with Cu-1106P was reduced to one third if the oil was subjected to degassing at 185 C prior to the charging of catalyst (11). The corresponding reduction of the reaction time t_{15} with Cu/SiO_2 (B) in the same rapeseed oil was only ca. 20% (33 to 27 minutes). The poisoning effect of volatile oxidation products is thus considerably lower with the use of Cu/SiO_2 catalysts.

Concerning the selectivity S_{Ln} , there is no difference between the four tested catalysts.

Product Evaluation

A sample of the rapeseed oil type Lowbra was hydrogenated in the test-autoclave (4 x 300 g) with the catalyst mixture D. The

product obtained was evaluated for fatty acid composition and organoleptic quality. The process conditions were as follows: 0.1 wt-% Cu in the oil, 185 C, 6 atm, 1 700 rpm, and 50 liter H_2 /hr. The reaction was interrupted after 35 minutes. The oil was cooled and filtered through Celite. Citric acid was added in an amount corresponding to 120 ppm. The hydrogenated oil was bleached and deodorized together with a reference sample, consisting of original bleached rapeseed oil.

The hydrogenation process included an iodine value decrease from 108.7 to 95.8 (method according to Hanus). The change of fatty acid composition is shown in Table III, which also includes the anisidine values (AV), the peroxide values (PV), free fatty acid values (FFA), and the colour values (Lovibond 5 1/4") of the reference substance and the Cu-hydrogenated oil, both after bleaching and deodorization. The selectivity S_{Ln} towards the linolenate was 7.1. The copper content of the oil at different stages during processing changed according to Table IV (atomic absorption spectroscopy).

The Cu-hydrogenated rapeseed oil was compared to the reference substance by a taste-panel in a short-time test. According to the procedure used, the oil samples were kept in open pots at 50 C between the flavour evaluations (Table V).

No hydrogenation taste was found. The hydrogenation step increased the oil stability towards oxidation even if the difference between the hydrogenated and unhydrogenated oil was smaller than expected with the low linolenate content in

thought. However, the result is consistent with new findings that a good quality raw oil, which is carefully refined and deodorized, often shows good stability towards oxidation even without a hydrogenation step.

The removal of catalyst copper from the oil causes no problems. Bleaching with a citric acid addition reduces the copper content beyond the level of detection, 0.004 ppm.

DISCUSSION

The similarities between the behaviour of the copper chromite catalyst and the Cu/SiO_2 catalyst containing ca. 17% Cu are obvious. This condition could mainly be ascribed to the fact that the copper of the two catalysts is charged into the oil in its divalent state and that the reduction of the copper during the hydrogenation proceeds through the same degrees of oxidation. The reduction potential is influenced by the hydrogen concentration of the oil, which is nearly proportional to the hydrogen pressure in the gaseous phase. Independent of the material charged, water is generated during the catalyst reduction, and the effect of catalyst poisoning is to be found as long as this reduction water remains within the oil phase.

Concerning the relation between the surface properties and the hydrogen pressure, the Cu/SiO_2 catalyst is somewhat different from the previously studied copper chromite catalyst. The maximum of the reaction rate about 6 atm is sharper and

the reduced catalyst does not contribute in any greater extent to the activity during the first t_{15} minutes until the pressure is increased to about 14 atm. The conclusions previously drawn concerning the active phase of copper in the hydrogenation of vegetable oils, based on the experimental work with the copper chromite catalyst, may be supplemented and summarized as follows:

The Cu^{II} ions of the copper chromite and the Cu/SiO_2 surfaces are not resistant to reduction, thus the active phases must consist of Cu^{I} compounds and/or Cu^0 . Judging from the changes of the catalyst activity during the hydrogenation at low pressure levels, activity is first obtained from the catalyst subjected to reduction and then eventually from the metal-reduced form of catalyst, i.e. $\text{Cu}/\text{Cr}_2\text{O}_3$ and Cu/SiO_2 of which a minor part of the copper still is bonded chemically to the oxidic supports. A surface consisting of only Cu^0 atoms, which thus represents the totally reduced surface without any support effect, shows low activity

Thus, two active phases are indicated. In the hydrogenation with unused catalyst, the transition from the oxidic phase, where the major part consists of Cu^{I} , to the metallic phase occurs after a reduction period of 50-60 minutes at 3 atm H_2 pressure. The contribution of the oxidic phase to the activity of the catalyst decreases with increasing pressure. At higher pressure levels (~ 10 -30 atm), the metallic copper on an oxidic support (Cr_2O_3 or SiO_2), containing a small amount of Cu^{I} , is the active phase used after a short induction period.

In contrast to the reduced form of the catalyst, the oxidic catalyst phase gives a temporary accumulation of conjugated dienes in the oil. This is the result of an initial excess of oxidic sites which adsorb fatty molecules and where the conjugation reaction occurs. Also the conjugation reaction requires the presence of adsorbed hydrogen, which may explain the necessary contribution of Cu^0 promoted by the support, i.e. the hydrogen adsorbing component of the reaction model and the one which attends the hydrogen addition reaction. During a hydrogenation process in the low pressure region ($\sim 2-10$ atm) including an iodine value drop of 15 units in 40-60 minutes with unused catalyst, the oxidic component is the limiting factor. This is clear from the experiments with different conditions of Cu adsorption and with the catalyst mixtures. A stronger bonding between the copper content and the SiO_2 support gives a better exploitation of the copper at the first use of the catalyst. The optimal catalyst mixture contains 2/3 of the copper content as tighter bonded copper.

The Cu/SiO_2 and the copper chromite catalysts are rather equivalent in soybean oil processing, while the former type of catalyst is superior in rapeseed oil hydrogenation. To what extent the difference in rapeseed oil is dependent on the fact that the copper content of Cu/SiO_2 is more resistant to reduction, according to the X-ray diffraction analyses, is not fully clear. However, part of the difference found depends on the varying resistability to catalyst poisoning.

The maximum rate of hydrogenation with unused Cu/SiO_2 catalyst in the pressure interval up to 30 atm is obtained at 6 atm.

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Technical assistance by Mrs. Birgitta Svensson. Continuous interest in this investigation by Professor Sten T. Lundin is greatly appreciated. The product evaluation was performed at KARLSHAMNS, Sweden. Financial support given in part by the Swedish Board for Technical Development.

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TABLE I

A comparison between the Cu-1106P and Cu/SiO₂ catalysts in the hydrogenation of soybean and rapeseed oils (6 atm and 185 C).

Oil	Catalyst ^a	C _{Cu} ^b %	t ₁₅ min	$\frac{100}{t_{15} \cdot C_{Cu}}$ min ⁻¹	S _{Ln}
Soybean	A	0.20	21	24	9.7
oil	B	0.15	30	22	9.8
Rapeseed	A	0.20	83	6	6.8
oil	B	0.15	34	20	7.5

^a A = Cu-1106P; B = Cu/SiO₂ - 16.8 % Cu

^b C_{Cu} = wt-% Cu in the oil

TABLE II

A comparative catalyst test in rapeseed oil at 6 atm and 185 C.

Catalyst ^a	Amount of catalyst g/300 g	C _{Cu} ^b %	t ₁₅ min	$\frac{100}{t_{15} \cdot C_{Cu}}$ min ⁻¹	S _{Ln}
A	1.2	0.12	120	7	5.0
B	1.8	0.10	55	18	5.3
C	3.0	0.10	40	25	5.3
D	4.4	0.10	62	16	5.3

^a A = Cu-1106P, B = Cu/SiO₂ - 16.8 % Cu, C = Cu/SiO₂ - 10.1 %, and D = Cu/SiO₂ (mixture) - 6.7 % Cu.

^b C_{Cu} = wt-% Cu in the oil

TABLE III

Fatty acid composition and other data of unhydrogenated and Cu-hydrogenated rapeseed oils in the product evaluation test.

Oil	Reference oil, bleached	Cu-hydr. oil, bleached	Reference oil, deod.	Cu-hydr. oil, deod.
IV (Hanus)	108.7	95.8		
<u>GLC</u>				
C16:0			4.1	4.2
C18:0			1.8	1.7
C18:1			60.3	69.4
C18:2			19.7	19.3
C18:3			8.2	0.5
C20:0			1.1	0.7
C20:1			3.1	2.4
C22:1			0.5	0.3
AV	2.0	0.4	1.3	0.4
PV	0.0	0.0	0.0	0.0
FFA	0.07	0.12		
Colour	$\left\{ \begin{array}{l} 7.0 \times 1.2 = \\ 19.0 \end{array} \right.$	$\left\{ \begin{array}{l} 1.8 \times 0.7 = \\ 8.8 \end{array} \right.$	$\left\{ \begin{array}{l} 2.0 \times 0.6 = \\ 8.0 \end{array} \right.$	$\left\{ \begin{array}{l} 2.0 \times 0.6 = \\ 8.0 \end{array} \right.$

TABLE IV

Copper content of the rapeseed oil used in the product evaluation.

Oil	Cu content, ppm
Raw oil	0.04
Oil before hydrogenation	0.005
Cu-hydrogenated oil after filtering	0.20
Cu-hydrogenated oil after bleaching	< 0.004
Reference oil after bleaching	< 0.004

TABLE V

Flavor stability of Cu-hydrogenated rapeseed oil.

Days, 50 C	Flavor scores ^a	
	Ref. oil, deod.	Cu-hydr. oil deod.
0	4.7	5.3
1	4.0	3.8
3	3.0	3.6

^a Scores 1-7, 7 = Oil free from flavor and odor



FIG: 1. MS-Gel 951 (a) and Cu/SiO₂ catalyst containing 17%

Cu (b).

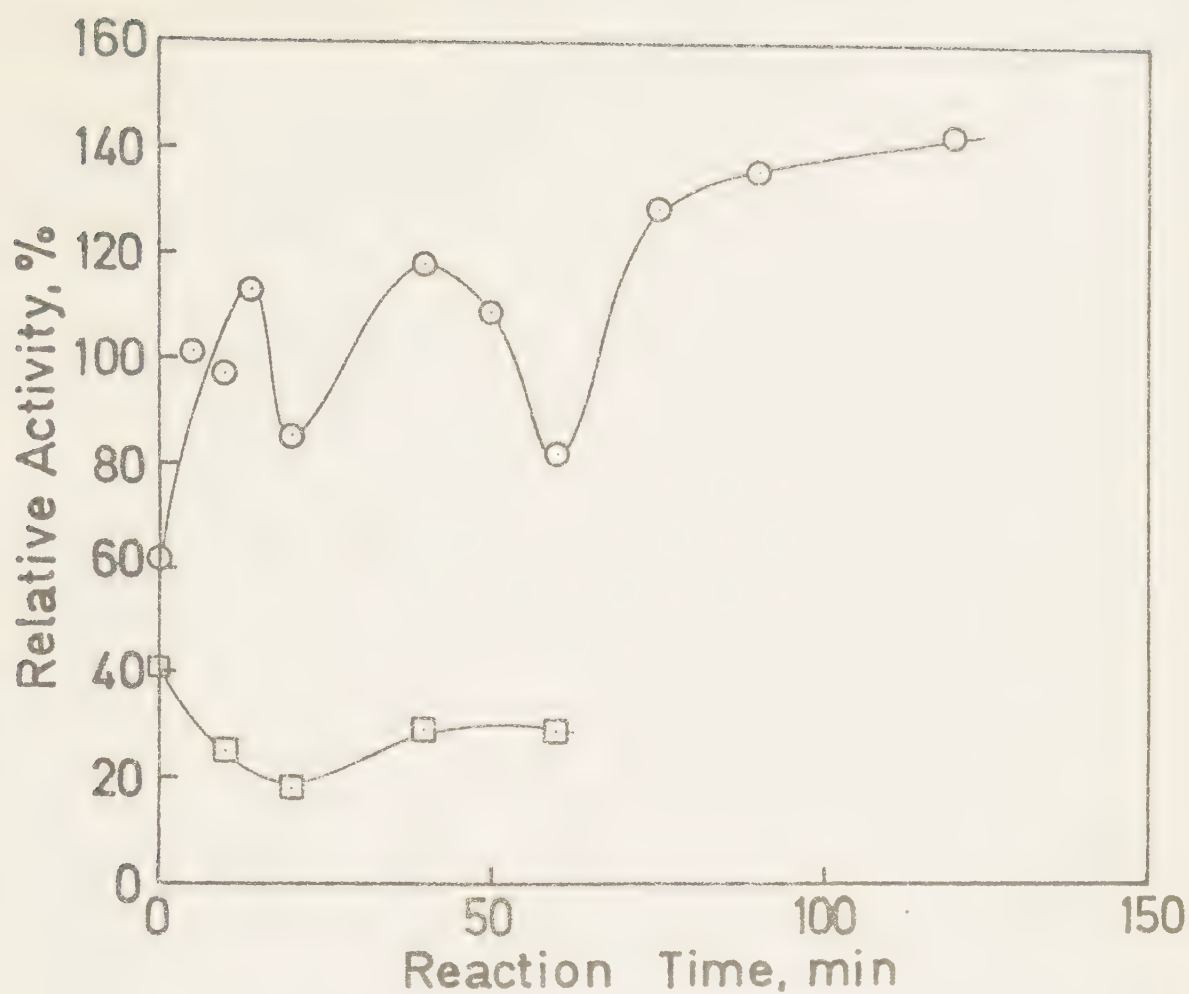


FIG. 2. Relative activity of the Cu/SiO_2 catalyst (17% Cu) according to the direct measurement after its use in soybean oil at 3 atm/185 C (O) and in rapeseed oil at 6 atm/185 C (□); 0.10 and 0.15 wt-% Cu in the oil resp. and $y = 3.0$.

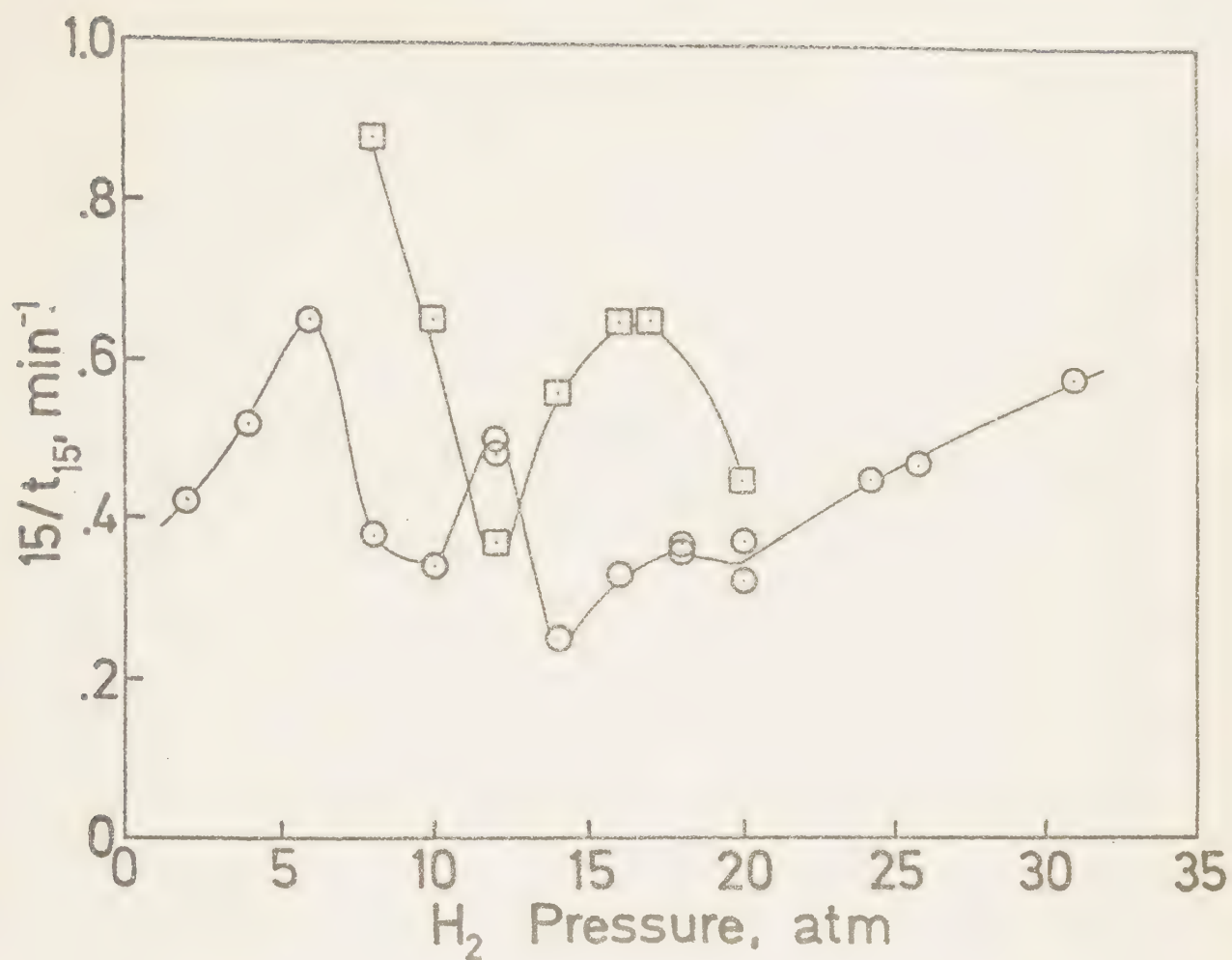


FIG. 3. Effect of hydrogen pressure on the mean rate of reaction in the hydrogenation of rapeseed oil at 185 C (O) and 200 C ($\square$); Cu/SiO₂ (17% Cu) and 0.12 wt-% Cu in the oil.

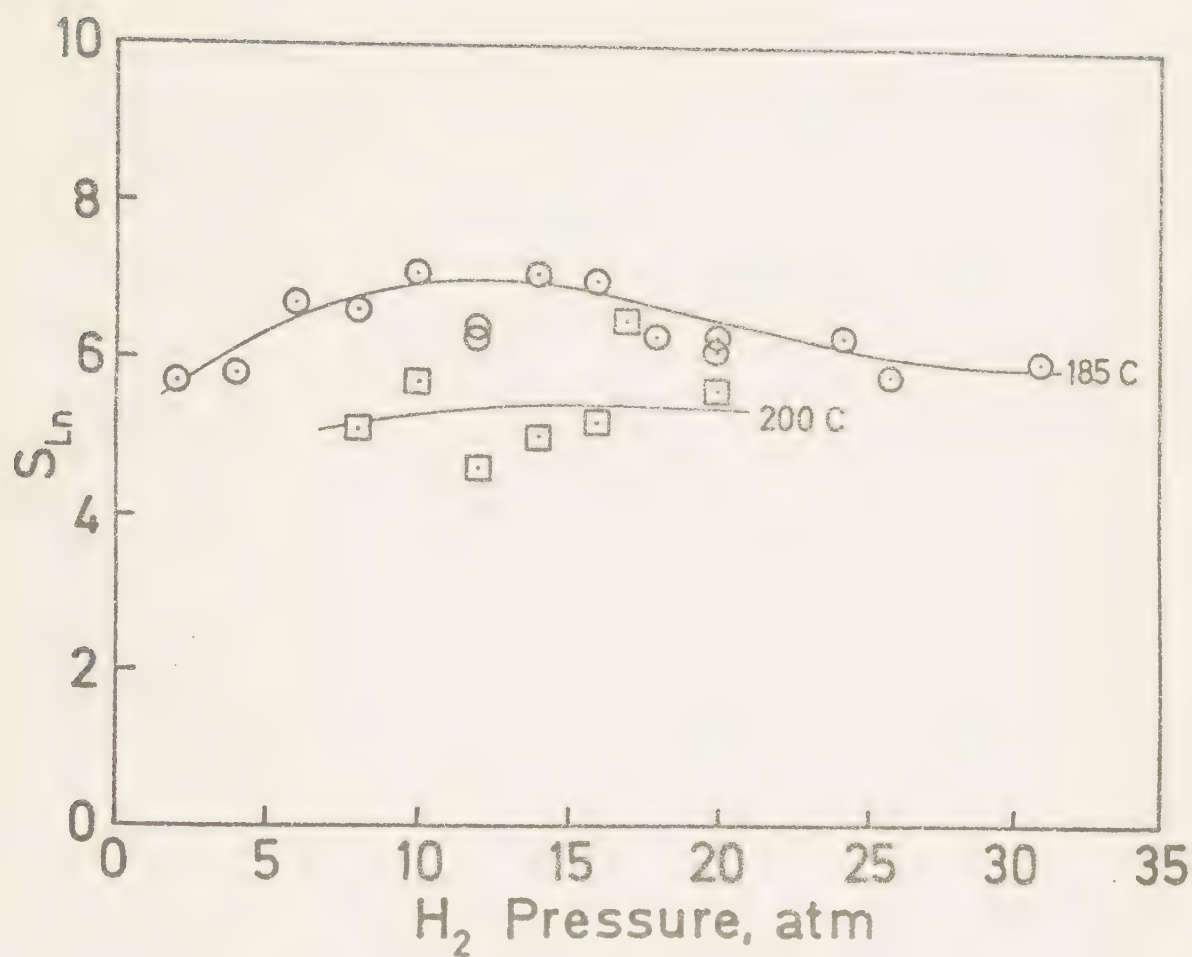


FIG. 4. Effect of hydrogen pressure on the selectivity S_{Ln} at hydrogenation of rapeseed oil; Cu/SiO₂ (17% Cu) and 0.12 wt-% Cu in the oil.

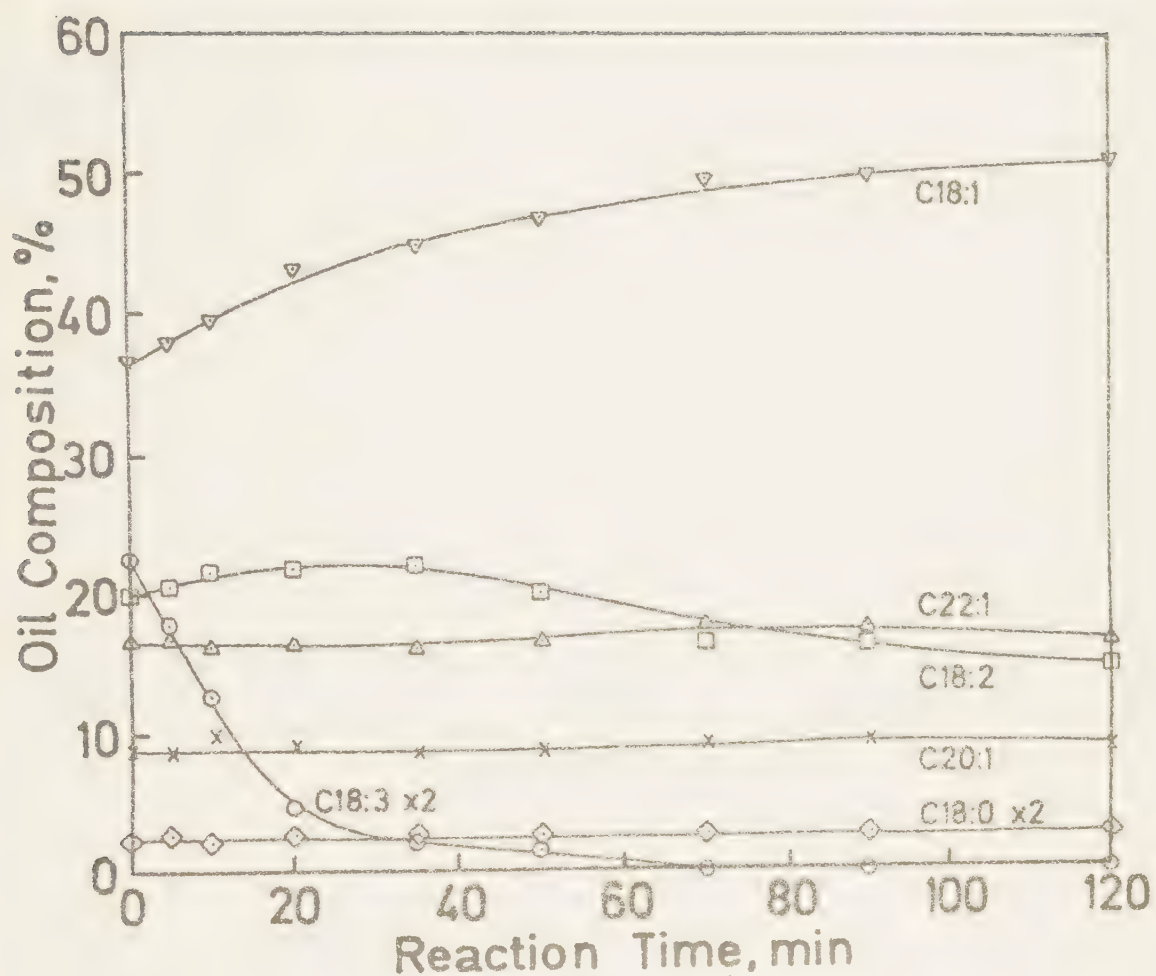


FIG. 5. The GLC-composition of rapeseed oil during hydrogenation with Cu/SiO_2 (17% Cu) at 6 atm and 185 C; 0.12 wt-% Cu in the oil.

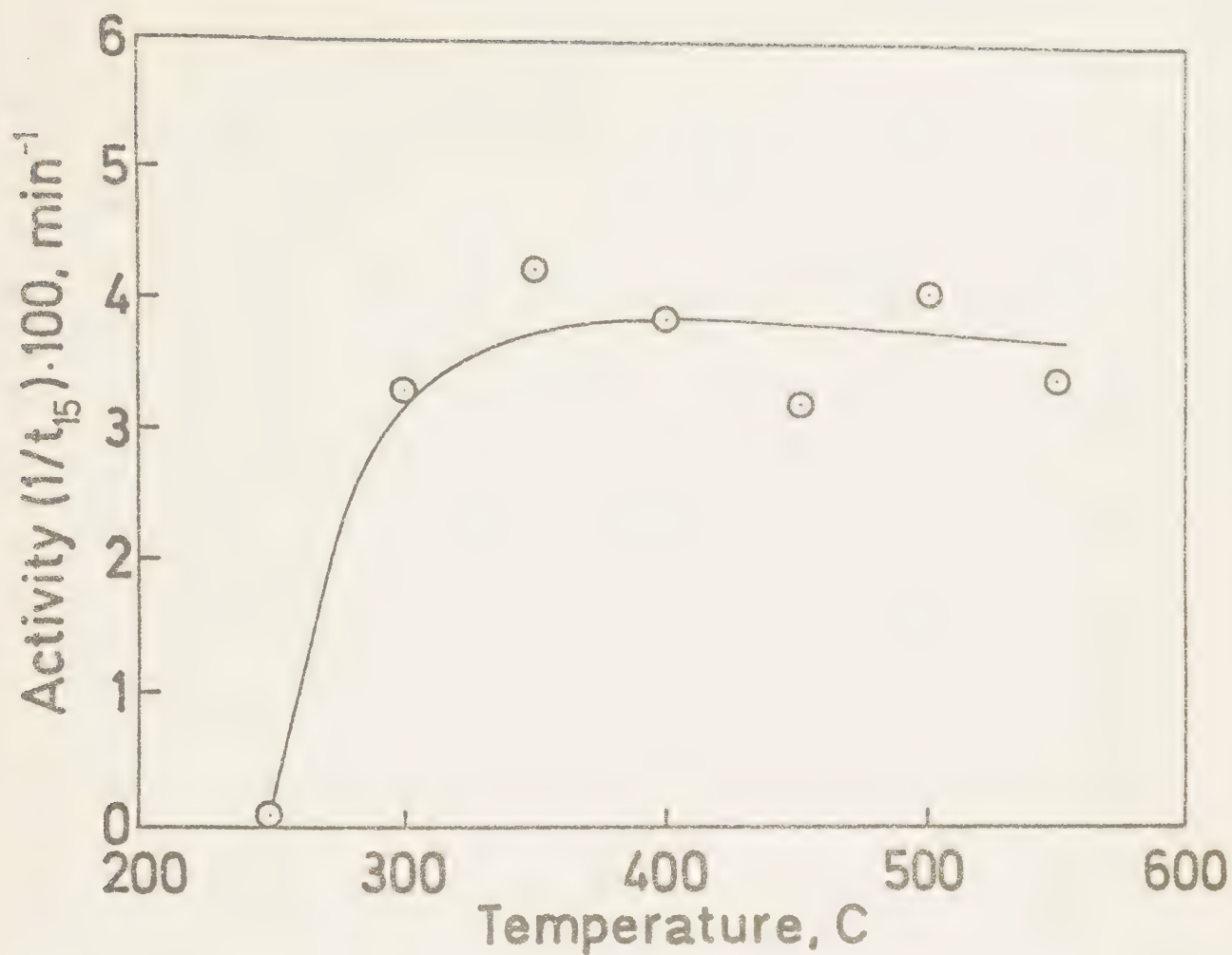


FIG. 6. The effect of the calcination temperature on the activity of Cu/SiO_2 (17% Cu). The catalyst material tested in soybean oil at 6 atm and 185 C; 0.15 wt-% Cu in the oil.

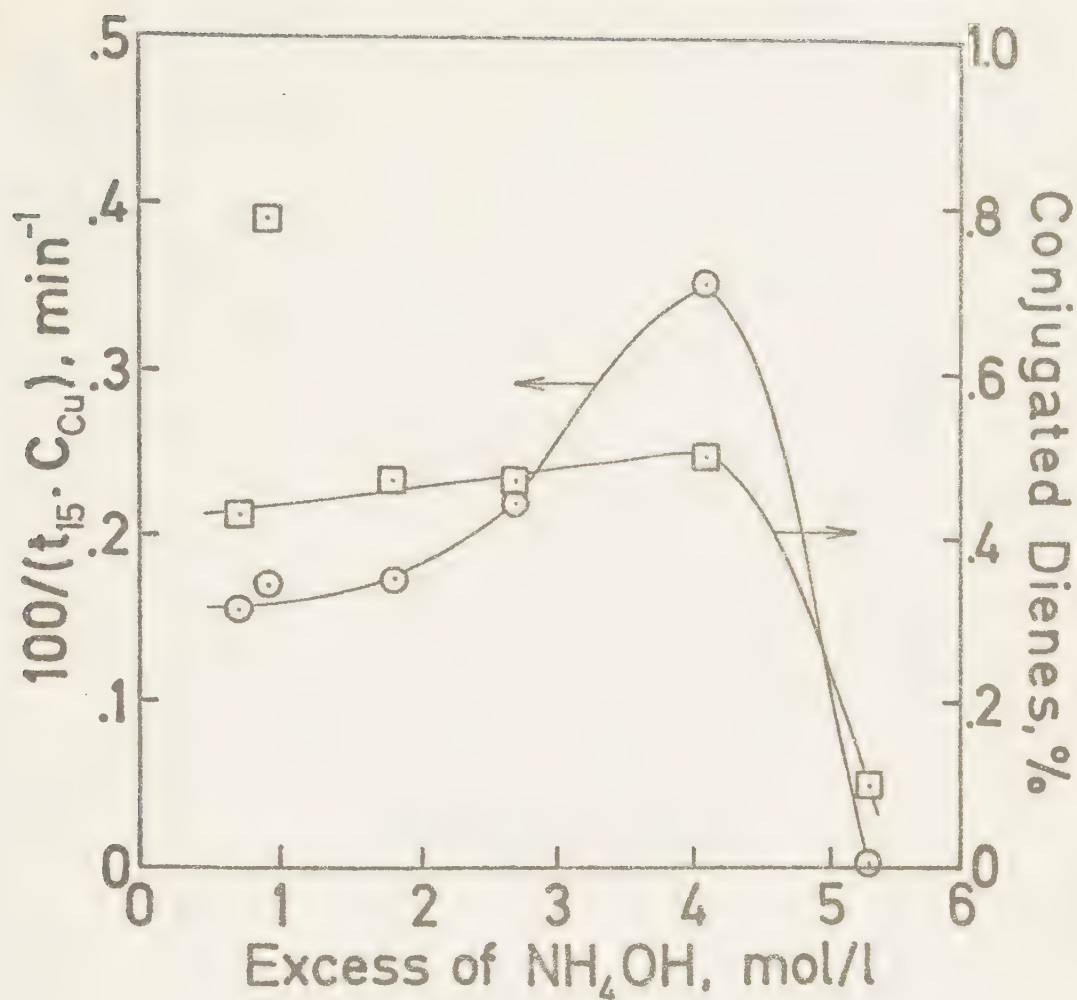


FIG. 7. Catalyst activity per wt-% Cu in the oil as a function of the NH_4OH excess in the adsorption solution; rapeseed oil hydrogenation at 6 atm and 185 C.

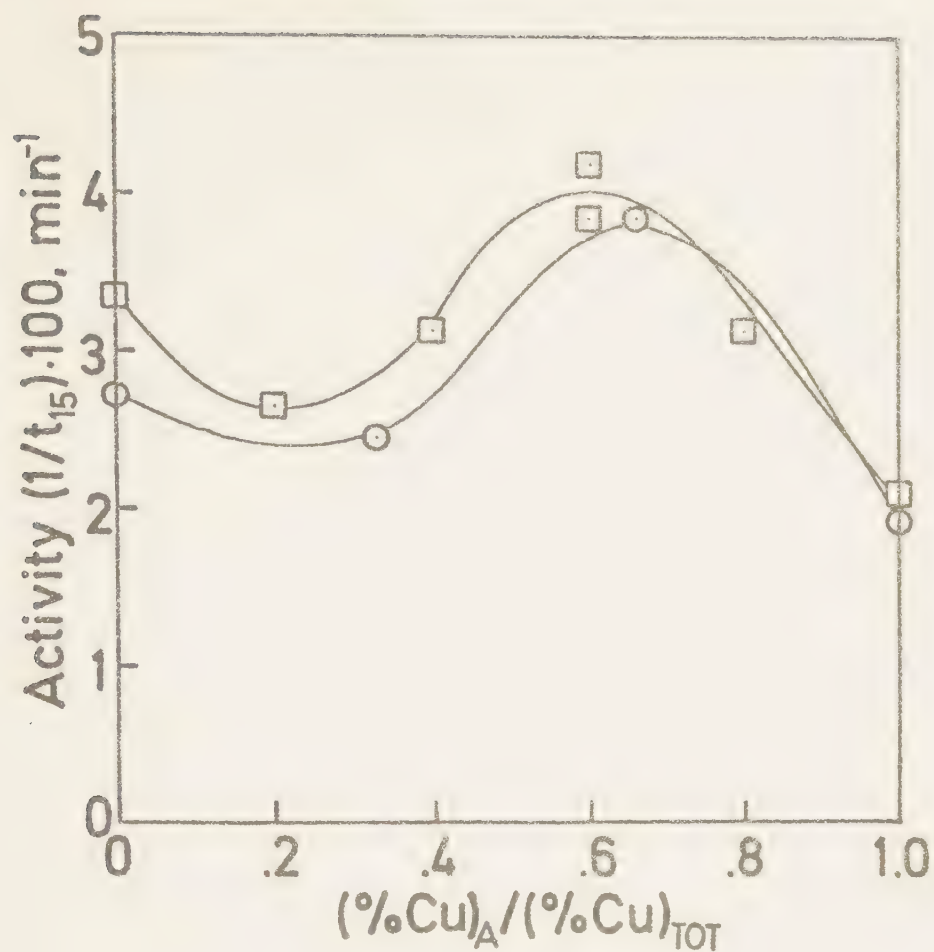


FIG. 8. Catalyst activity versus the fraction of copper charged as catalyst Type A, containing 4% Cu (0.15 wt-% Cu in rapeseed oil, 6 atm, and 185 C).

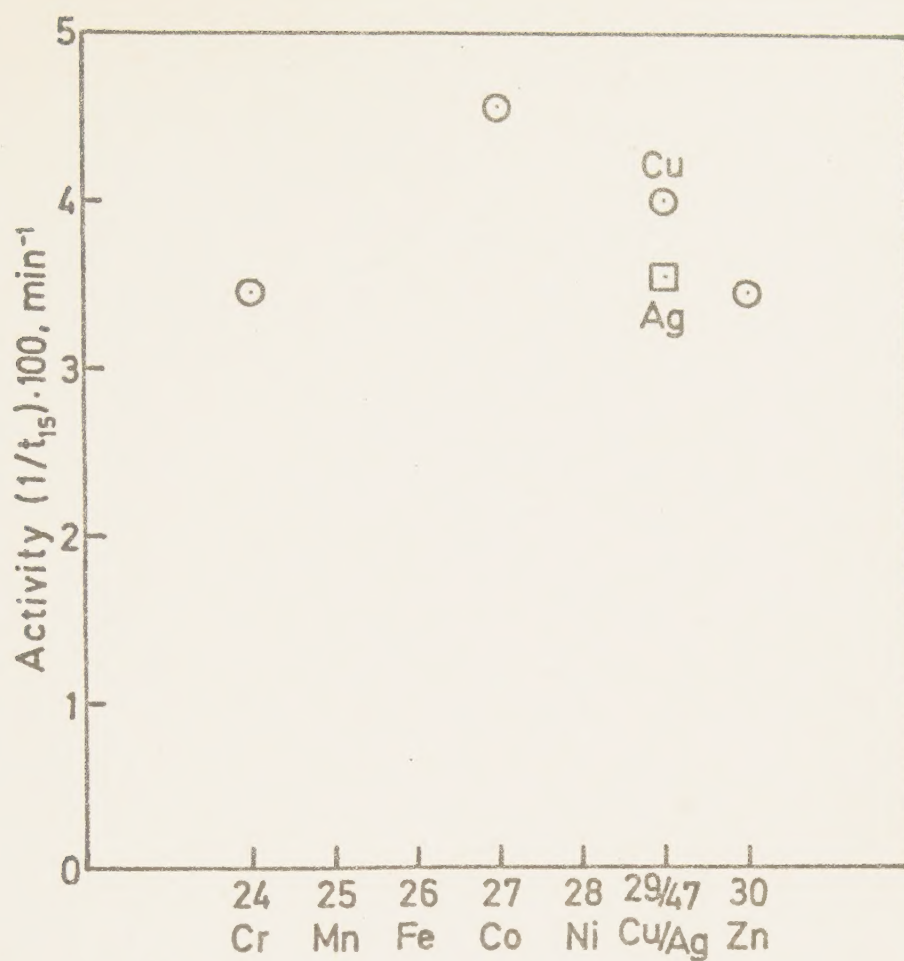


FIG. 9. Promoted Cu/SiO₂ catalyst (0.13 wt-% Cu in soybean oil, 6 atm, and 185 C).



FIG. 2. Predicted rainfall, based on the 1971-72 season. The predicted rainfall, based on the 1971-72 season, is shown in the figure.

